

## Relative vibrational transition probabilities in the ( $B^3 \pi_g - A^3 \Sigma_u^+$ ) system of nitrogen for Hulbert-Hirschfelder oscillator model

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**Abstract.** Hulbert-Hirschfelder (H-H) potential function has been used to obtain the relative vibrational transition probabilities for the observed bands of the first positive system of nitrogen molecule. The vibrational wavefunctions have been calculated by solving the Schrödinger equation by the method due to Langer, at low vibrational quanta and by the wkb method at high vibrational quanta. It is established that the H-H potential is superior to the often used Morse potential function for the transition under consideration.

**Keywords.** Relative transition probabilities; Hulbert-Hirschfelder potential;  $N_2$  ( $B^3 \pi_g - A^3 \Sigma_u^+$ ) system.

### 1. Introduction

The theoretical prediction of intensity distribution in the molecular band system requires the knowledge of transition probabilities which are to a good approximation proportional to the Franck-Condon (F-C) factors  $\langle V' | V'' \rangle^2$  where  $|V'\rangle$  and  $|V''\rangle$  are the vibrational eigenfunctions of the upper and lower electronic states of the transition. It has been almost customary to use the Morse oscillator model since the exact vibrational eigenfunctions are known. However, it is known that this model performs badly (Steel *et al* 1962) for the ( $B^3 \pi_g - A^3 \Sigma_u^+$ ) system of nitrogen. The FC factors are model sensitive and, therefore, we have endeavoured to test other models for the above band system. In the present work the H-H oscillator model has been investigated.

### 2. Potential function

The Hulbert-Hirschfelder potential function is given by (Hulbert and Hirschfelder 1941)

$$U(r) = D_e [1 - \exp(-ax)]^2 + ca^3 x^3 [\exp(-2ax)] (1 + bax),$$

where  $a = w_e/2 (B_e D_e)^{1/2} r_e \text{ cm}^{-1}$ ,  $x = (r - r_e) \text{ cm}$ ,

$$c = 1 + a_1 (D_e/a_0)^{1/2}; b = 2 - [(7/12) - (D_e a_2/a_0)]/c$$

with  $a_0 = w_e^2/4B_e$ ,  $a_1 = -1 - (\alpha_e w_e/6B_e^2)$ ,  $a_2 = 5a_1^2/4 - 2/3 (w_e x_e/B_e)$ .

The other undefined symbols have their usual meanings (Herzberg 1950). The turning point values for this potential have been calculated using the spectroscopic constants given by Herzberg (1950) and the results are given in tables 1a and 1b.

### 3. Calculation of FC factors

At low quantum numbers the normalised eigenfunctions have been obtained using the method due to Langer as adopted by Tawde and Itagi (1967). At high quantum numbers the wkb method (Wu 1952) was used. Near the turning points (singular points for the wkb approximation) the linear approximation due to Langer (1937) was used. These solutions are given in terms of Bessel functions of the order  $\pm 1/3$  with both real and imaginary arguments and the values are taken from NBS monograph (1948). The method due to Langer and the wkb approximation are complementary to each other and hence all the wavefunctions are expected to be more reliable. The overlap integrals were computed by numerical integration. The results have been recorded in table 2. The values obtained using the Morse oscillator model (Jarman and Nicholls 1952) have also been recorded for comparison.

**Table 1a.** Turning points for Hulbert-Hirschfelder potential  $B^2\pi_g$ .

$v$	$r \text{ \AA}$ minimum	$r \text{ \AA}$ maximum
2	1·109 <sub>8</sub>	1·349 <sub>7</sub>
3	1·094 <sub>0</sub>	1·379 <sub>0</sub>
4	1·081 <sub>0</sub>	1·407 <sub>5</sub>
5	1·069 <sub>8</sub>	1·433 <sub>5</sub>
6	1·060 <sub>5</sub>	1·458 <sub>5</sub>
7	1·051 <sub>3</sub>	1·482 <sub>6</sub>
8	1·043 <sub>5</sub>	1·506 <sub>3</sub>
9	1·036 <sub>3</sub>	1·529 <sub>5</sub>
10	1·029 <sub>7</sub>	1·552 <sub>4</sub>
11	1·023 <sub>6</sub>	1·575 <sub>2</sub>
12	1·018 <sub>4</sub>	1·597 <sub>0</sub>

**Table 1b.** Turning points for Hulbert-Hirschfelder potential  $A^2\Sigma_u^+$ .

$v$	$r \text{ \AA}$ minimum	$r \text{ \AA}$ maximum
2	1·178 <sub>6</sub>	1·440 <sub>6</sub>
3	1·160 <sub>2</sub>	1·472 <sub>0</sub>
4	1·144 <sub>0</sub>	1·502 <sub>6</sub>
5	1·131 <sub>6</sub>	1·530 <sub>3</sub>
6	1·119 <sub>8</sub>	1·557 <sub>1</sub>
7	1·099 <sub>5</sub>	1·583 <sub>2</sub>
8	1·099 <sub>6</sub>	1·608 <sub>7</sub>

Table 2. Comparison of theoretical and experimental transition probabilities for the observed bands of the first positive system of  $N_2$ .

$v'$ \ $v''$	0	1	2	3	4	5	6	7	8
0	1.000 1.000 (1.000)	0.950 0.957 (0.829)	0.559 0.530 (0.624)						
1	1.000 1.000 (1.000)		0.254 0.323 (0.655)	0.436 0.473 (0.860)	0.364 0.357 (1.109)				
2	0.943 0.821 (0.516)	1.000 1.000 (1.000)	0.533 0.432 (0.412)	0.009 0.952 (0.357)	0.349 0.546 (0.836)	0.594 0.694 (1.139)			
3	0.166 0.159 (0.139)	1.000 1.000 (1.000)	0.129 0.201 (0.586)	0.535 0.550 (0.842)	0.103 0.038 (0.568)	0.030 0.142 (0.967)	0.229 0.394 (2.044)		
4		0.491 0.409 (0.257)	1.000 1.000 (1.000)	0.003 0.003 (0.167)	0.414 0.503 (0.721)				
5		0.147 0.087 (0.058)	1.141 0.904 (0.579)	1.000 1.000 (1.000)		0.239 0.372 (0.737)			
6		0.012 0.008 (0.012)	0.228 0.220 (0.146)	1.000 1.000 (1.000)	0.320 0.576 (0.961)	0.413 0.263 (0.524)			
7			0.030 0.019 (0.018)	0.383 0.291 (0.220)	1.000 1.000 (1.000)	0.074 0.254 (0.451)	0.476 0.354 (0.681)		
8				0.075 0.033 (0.043)	0.671 0.444 (0.343)	1.000 1.000 (1.000)			
9					0.186 0.059 (0.067)	1.069 0.539 (0.500)	1.000 1.000 (1.000)		
10						0.415 0.139 (0.109)	1.754 0.885 (0.727)	1.000 1.000 (1.000)	
11							0.315 0.118 (0.174)	1.000 1.000 (1.000)	0.220 0.786 (0.870)
12								0.434 0.219 (0.222)	1.000 1.000 (1.000)

Note: The experimental values given in parentheses are scaled such that the value for the intense band of each  $v'$ -progression is equal to one.

1st value is Morse  $q_{v',v''}$ .

2nd value is Hulbert-Hirschfelder  $q_{v',v''}$ .

Bracketted values:  $R_{v',v''}^E$ -Experimental T.Ps. (Turner and Nicholls 1954).

#### 4. Comparison with experimental intensities

The integrated intensity of a band is given by

$$I_{\nu', \nu''} = K N_{\nu'} \nu_{\nu', \nu''}^A \bar{R}_e^2 q_{\nu', \nu''},$$

with  $q_{\nu', \nu''} = \langle \nu' | \nu'' \rangle^2$ .

The constant  $K$  contains the factors depending on the choice of units and the geometry of the experimental set up.  $N_{\nu'}$  is the vibrational population of the upper state,  $\nu_{\nu', \nu''}$  is the frequency of the band origin.  $\bar{R}_e^2$  is the average electronic transition moment assumed to be constant. If one considers the relative intensity distribution in a  $\nu''$  progression the  $N_{\nu'}$  may be taken to be fairly constant. Under these circumstances  $I/\nu_{\nu', \nu''}^A$  is proportional to  $q_{\nu', \nu''}$ . On this basis it is possible to compare the theoretically calculated FC factors and the experimentally determined band intensities. Following this procedure  $I/\nu_{\nu', \nu''}^A$  values have been calculated using the experimental data reported by Turner and Nicholas (1954). These values have also been entered in table 1. The normalisation has been carried out with respect to the intense band in a given  $\nu''$  progression.

#### 5. Conclusions

From the study of the relative values of the theoretical FC factors and the experimental data it is evident that the H-H oscillator model is quite superior to the Morse oscillator model. It is worth noting that at high quantum numbers the H-H model gives better performance, thereby proving that it is a very good model to represent the  $B^3 \pi_g$  and  $A^3 \Sigma_u^+$  states of  $N_2$ .

In conclusion we may add that it is necessary to explore various empirical potential functions and an exhaustive study will help to understand the molecular structure better.

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