Theoret. chim. Acta (Berl.) 18, 162—165 (1970)

Relationes

Franck-Condon Factors for the Transitions N_2, $C^3\pi_u \rightarrow B^3\pi_g$ and CN, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ★

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Received May 5, 1970

Franck-Condon factors for the transitions N_2, $C^3\pi_u \rightarrow B^3\pi_g$ and CN, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ have been calculated by the method of Chang and Karplus.

The Franck-Condon factor, $q_{v'v''}$, plays a very important role in the determination of intensity distributions in a system of electronic vibrational bands of a diatomic molecule [1]. It is defined as the square of the overlap integrals of the vibrational wavefunctions $\psi_{v'}$ and $\psi_{v''}$ of the upper and lower electronic states, respectively,

$$q_{v'v''} = |I_{v'v''}|^2 = \left| \int_0^\infty \psi_{v'}(r)\, \psi_{v''}(r)\, dr \right|^2 . \tag{1}$$

Various methods [2–5] have been proposed for calculations of Franck-Codon factors. However, all the methods given the literature suffer some shortcomings. They are only appropriate for particular ranges of vibrational quantum numbers and some of the methods involve a laborious calculation. Recently, Chang and Karplus [6] have introduced the asymptotic expansion method for Franck-Condon factor calculations. In the present note, this method is applied to the second positive ($C^3\pi_u \rightarrow B^3\pi_g$) band system of N_2 and the violet system of CN($B^2\Sigma^+ \rightarrow X^3\Sigma^+$). Double precision computations have been carried out on a CDC 6600 computer. The results which are in excellent agreement with the values obtained by the extremely tedious method of numerical integration of accurately computed Morse wave functions, over a much larger range of vibrational quantum numbers than has been previously reported [2–5] are shown in Tables 1 and 2. These more extensive data have been found useful in the interpretation of laboratory spectra where large vibrational quantum numbers are often encountered. Besides, we have found that the method of Chang and Karplus gives accurate results for a wide range of vibrational quantum numbers for which a Morse potential can be expected to be valid. Also, the method is very simple to use. For v' or v'' greater than ten cases, it requires more than 20 significant figures, so double precision computations on CDC 6600 are recommended.

★ This research was supported by the Office of Naval Research under Contract # N00014-69-A-0453.

Table 1. *Values of* $q_{v'v''}$ *of* $C^3\pi_u \rightarrow B^3\pi_g$ *of* N_2

v'' \ v'	0	1	2	3	4	5	6	7	8	9	10	11	12
0	0.4493	0.3899	0.1349	0.0236	0.0022	0.0001							
	(0.448)	(0.393)	(0.135)	(0.022)	(0.002)								
1	0.3287	0.0187	0.3223	0.2515	0.0696	0.0088	0.0005						
	(0.328)	(0.019)	(0.323)	(0.256)	(0.070)								
2	0.1469	0.2038	0.0330	0.1630	0.3034	0.1273	0.0211	0.0015					
	(0.146)	(0.203)	(0.032)	(0.163)	(0.303)								
3	0.0523	0.2003	0.0596	0.1181	0.0475	0.2942	0.1852	0.0394	0.0033	0.0001			
	(0.053)	(0.195)	(0.062)	(0.116)	(0.048)								
4	0.0163	0.1124	0.1614	0.0018	0.1570	0.0020	0.2449	0.2347	0.0631	0.0061	0.0002		
	(0.016)	(0.115)	(0.158)	(0.002)	(0.156)								
5	0.0047	0.0484	0.1427	0.0889	0.0142	0.1411	0.0098	0.1785	0.2699	0.0911	0.0102	0.0003	
	(0.005)	(0.047)	(0.142)	(0.092)	(0.018)								
6	0.0013	0.0179	0.0830	0.1345	0.0294	0.0536	0.0962	0.0439	0.1129	0.2891	0.1219	0.0157	0.0005
	(0.001)	(0.020)	(0.082)	(0.141)	(0.032)								
7	0.0003	0.0060	0.0386	0.1062	0.0995	0.0020	0.0873	0.0486	0.0820	0.0594	0.2926	0.1540	0.0225
		(0.006)	(0.039)	(0.107)	(0.098)								
8	0.0001	0.0019	0.0156	0.0616	0.1105	0.0567	0.0046	0.1004	0.0149	0.1102	0.0229	0.2828	0.1859
		(0.001)	(0.016)	(0.057)	(0.118)								
9		0.0006	0.0058	0.0298	0.0802	0.0965	0.0218	0.0247	0.0924	0.0006	0.1227	0.0040	0.2626
		(0.001)	(0.006)	(0.024)	(0.077)								
10		0.0002	0.0002	0.0128	0.0461	0.0892	0.0707	0.0030	0.0485	0.0705	0.0038	0.1199	0.0003
			(0.002)	(0.015)	(0.040)								
11			0.0007	0.0051	0.0229	0.0611	0.0863	0.0421	0.0010	0.0658	0.0441	0.0184	0.1054
			(0.001)	(0.002)	(0.017)								
12			0.0002	0.0019	0.0103	0.0350	0.0711	0.0732	0.0182	0.0112	0.0719	0.0209	0.0376
				(0.002)	(0.010)								

The present results above graphical results from Ref. [4b] in parentheses; v' represents the upper vibrational level and v'' the low. The Morse function data are given in Ref. [4b].

Table 2. *Values of* $q_{v'v''}$ *of* $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ *of* CN

v'' \ v'	0	1	2	3	4	5	6	7	8	9	10	11	12
0	0.9201	0.0788	0.0011										
	(0.920)	(0.074)	(0.005)										
1	0.0742	0.7864	0.1369	0.0024									
	(0.079)	(0.787)	(0.121)	(0.014)									
2	0.0054	0.1206	0.6910	0.1795	0.0032	0.0002							
	(0.001)	(0.137)	(0.691)	(0.147)									
3	0.0003	0.0132	0.1474	0.6252	0.2101	0.0033	0.0004						
		(0.002)	(0.180)	(0.625)									
4		0.0009	0.0216	0.1603	0.5827	0.2309	0.0027	0.0009					
5			0.0019	0.0293	0.1634	0.5592	0.2431	0.0016	0.0015				
6				0.0030	0.0360	0.1592	0.5516	0.2472	0.0005	0.0023			
7				0.0002	0.0042	0.0414	0.1498	0.5577	0.2435		0.0031	0.0001	
8					0.0003	0.0054	0.0455	0.1363	0.5758	0.2317	0.0010	0.0038	0.0003
9						0.0004	0.0063	0.0486	0.1197	0.6042	0.2118	0.0044	0.0041
10							0.0005	0.0071	0.0508	0.1009	0.6412	0.1840	0.0107
11								0.0006	0.0075	0.0525	0.0806	0.6844	0.1994
12									0.0007	0.0076	0.0540	0.0599	0.7311

The present results above graphical results from Ref. [4a] in parentheses.

We are grateful to Drs. T. Y. Chang and M. Karplus for sending us their computer program and for helpful discussions (to T. Y. Chang). We also wish to thank Dr. Henry Maltz for reading the manuscript.

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