

Franck-Condon Factors to High Quantum Numbers VI: C_2 Band Systems

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Franck-Condon factor arrays have been computed numerically and are displayed to highest known vibrational quantum numbers for the following C_2 band systems:

Freymark	: ($e^1\Sigma_g^+ - b^1\Pi_u$)
Mulliken	: ($d^1\Sigma_u^+ - x^1\Sigma_g^+$)
Fox-Herzberg	: ($B^3\Pi_g - X'^3\Pi_u$)
Deslandres-d'Azambuja	: ($c^1\Pi_g - b^1\Pi_u$)
Swan	: ($A^3\Pi_g - X'^3\Pi_u$)
Phillips	: ($b^1\Pi_u - x^1\Sigma_g^+$)
Ballik-Ramsay	: ($A'^3\Sigma_g^- - X'^3\Pi_u$)

1. Introduction

In each of a number of previous papers, Franck-Condon factor arrays have been presented, molecule by molecule, for each of its common and important band systems: N_2 , N_2^+ [Nicholls 1961, 1962a]; CO^+ [Nicholls 1962b]; CN [Nicholls 1964a]; NO [Nicholls 1964b]; O_2 [Nicholls 1965]. In this paper Franck-Condon factor arrays are displayed for all important band systems of C_2 .

The C_2 molecule has important applications to astrophysics in the emission spectra from comets and in the absorption spectra from cool stars. It also has important applications to hydrocarbon combustion [Gaydon 1957]. There is thus a continuing demand for reliable transition probability data for various C_2 band systems. To this end, for example, Hagan [1963] has recently made measurements on the absolute oscillator strength of the (0,0) band of the Swan system. (See Metall and Nicholls [1965].)

The band systems of C_2 are listed with descriptive comments in table 1, and the transitions from which they arise are indicated on the simplified energy-level diagram of figure 1.

The discovery by Ballik and Ramsay [1959, 1960] that the true ground state of gaseous C_2 was $x^1\Sigma_g^+$ (the lowest state of the Phillips and Mulliken systems), rather than $X^3\Pi_u$ (the lowest state of the Swan system now designated $X'^3\Pi_u$) as had previously been assumed, has clarified our picture of the disposition of levels. The situation has been discussed in great detail by Ballik and Ramsay [1963a, b] and their designations of states are employed in

this paper. Perturbations in the $A'^3\Sigma_g^-$ state led them to locate $x^1\Sigma_g^+$ 610 cm^{-1} below $X'^3\Pi_u$. Perturbations in the $b^1\Pi_u$ state suggest the presence of the $A'^3\Sigma_u^+$ state from which no radiative transitions have yet been found.

TABLE 1. Band systems of C_2

Band system	Wavelength range (Å)	Reference
Freymark ($e^1\Sigma_g^+ - b^1\Pi_u$)	2072–2217	[1]
Mulliken ($d^1\Sigma_u^+ - x^1\Sigma_g^+$)	2313–2415	[2]
Fox-Herzberg ($B^3\Pi_g - X'^3\Pi_u$)	2378–3283	[3]
Deslandres-d'Azambuja ($c^1\Pi_g - b^1\Pi_u$)	3398–4102	[4]
Swann ($A^3\Pi_g - X'^3\Pi_u$)	4365–7853	[5, 6, 7]
Phillips ($b^1\Pi_u - x^1\Sigma_g^+$)	7715–12091	[8, 9]
Ballik-Ramsay ($A'^3\Sigma_g^- - X'^3\Pi_u$)	11726–24745	[10]

References

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|---------------------------------|---------------------------------|
| [1] Freymark (1951). | [6] Phillips (1948b). |
| [2] Landsverk (1939). | [7] Herzberg (1946). |
| [3] Phillips (1949). | [8] Phillips (1948a). |
| [4] Herzberg and Sutton (1940). | [9] Ballik and Ramsay (1963b). |
| [5] Johnson (1927). | [10] Ballik and Ramsay (1963a). |

2. Method

The straightforward method of computer calculation described in the first paper of this series [Nicholls 1961] was used to evaluate the arrays, and the calculations were performed at the Computation Center of The National Bureau of Standards.

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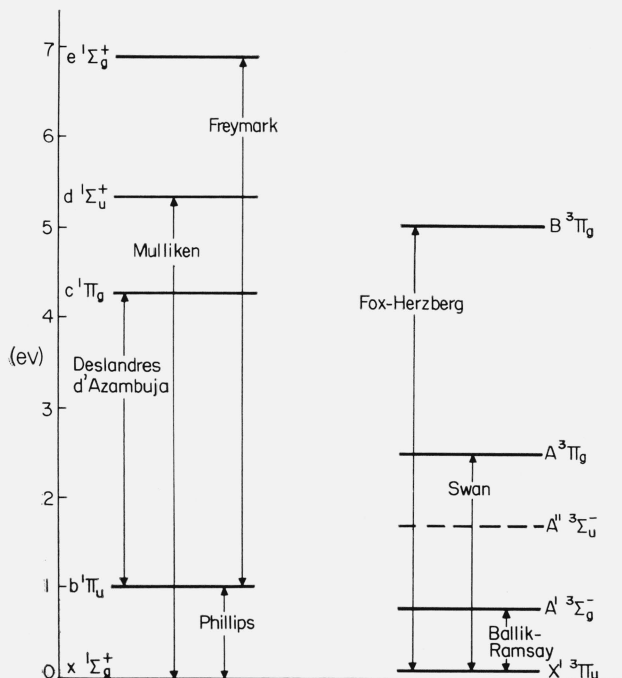


FIGURE 1. Partial energy level diagram for C_2 .

TABLE 2. Basic data

State	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$r_e(\text{\AA})$	v_{max}	Reference
$x^1\Sigma_g^+$	1854.71	13.34	1.24253	5	[1, 2]
$b^1\Pi_u$	1608.35	12.078	1.3184	8	[1, 2]
$c^1\Pi_g$	1809.1	15.81	1.2552	6	[1, 2]
$d^1\Sigma_u^+$	1829.57	13.97	1.2378	5	[1, 2]
$e^1\Sigma_g^+$	1671.5	40.02	1.2517	5	[1, 2]
$X^3\Pi_u$	1641.35	11.69	1.3119	13	[1, 2]
$A^3\Sigma_g^-$	1470.45	11.19	1.36928	4	[1, 2]
$A^3\Pi_g$	1788.22	16.44	1.2660	13	[1, 2]
$B^3\Pi_g$	1106.56	39.26	1.5350	4	[1, 2]

$$\mu_A = 6.00194$$

References

- [1] Ballik and Ramsay (1963b).
- [2] Wallace (1962).

Input data were ω_e , $\omega_e x_e$, r_e , v_{max} for both states and μ_A for the molecules. The notation is conventional [Herzberg 1950]. The Morse model was adopted for molecular potentials and the computer program provided for all needed vibrational wave functions and their overlap integral squares, the Franck-

Condon factors. The Morse potential is admittedly an empirical expedient, but the range of vibrational quantum numbers involved in most of the systems is low enough to justify its use. (See sec. 4. discussion.) The input data used in the calculations are summarized in table 2. Ballik and Ramsay's summary [1963b] of C_2 data and Wallace's [1962] compilations were used.

3. Results

Franck-Condon factor arrays are displayed in tables 3 through 9 for the band systems listed in table 1. The Condon loci [Nicholls 1963, Murty 1964] are indicated on the tables by setting the entries for bands which lie on local maxima of the Franck-Condon factor surface in bold faced type. The negative number in each entry is the power of ten by which it is multiplied.

4. Discussion

The Condon loci of tables 3 through 9 agree well with the $v'-v''$ positions of the commonly excited bands of each system [Pearse and Gaydon 1963, Wallace 1962], which is some justification of the adequacy of the potential model employed. In view of the importance of C_2 spectra to combustion studies some preliminary, limited ($v'+v'' \leq 6$) tables of Franck-Condon factors for C_2 systems of combustion importance were computed some years ago (Nicholls, Fraser, and Jarman [1959]) by the approximate method of Fraser and Jarman [1953]. The Mulliken, Deslandres-d'Azambuja, Phillips, Fox-Herzberg, and Swan systems of C_2 were treated as well as 14 band systems of other molecules. Basic data for these calculations were taken from Herzberg's [1950] compilation. A comparison between the entries of the limited approximate tables and those of this paper indicates that for the C_2 band systems treated the Franck-Condon factors were acceptable.

TABLE 4. Franck-Condon factors to high vibrational quantum numbers for the C_2 Mulliken ($d^1\Sigma_u^+ - X^1\Sigma_g^+$) system

v' \ v''	0	1	2	3	4	5
0	9.9659-1	3.2059-3	1.9741-4	7.8375-6	4.0407-7	2.4151-8
1	3.3154-3	9.9055-1	5.5526-3	5.5311-4	2.8989-5	1.8715-6
2	9.7176-5	5.9451-3	9.8573-1	7.1390-3	1.0339-3	6.6972-5
3	3.6867-7	3.0045-4	7.9164-3	9.8199-1	8.0604-3	1.6118-3
4	2.5241-9	1.5533-6	6.1685-4	6.1685-4	9.2616-3	9.7925-1
5	6.2444-10	7.9781-9	5.7079-6	1.0510-3	1.0019-2	9.7737-1

TABLE 3. Franck-Condon factors to high vibrational quantum numbers for the C_2 Freymark ($e^1\Sigma_g^+ - b^1\Pi_u$) system

v' \ v''	0	1	2	3	4	5	7	8	
0	5.4103-1	2.8232-1	1.1692-1	5.1251-2	1.3171-2	3.8774-3	1.0618-3	2.7011-4	6.3191-5
1	4.0076-1	1.1998-1	2.0714-1	1.5170-1	7.4629-2	3.0305-2	1.0731-2	3.4182-3	9.8891-4
2	5.7777-2	4.9616-1	2.6730-2	1.1897-1	1.4131-1	8.8599-2	4.3451-2	1.7778-2	6.3966-3
3	3.1770-5	9.9376-2	5.3176-1	1.0371-2	6.2287-2	1.2076-1	8.8321-2	5.0463-2	2.3012-2
4	3.9811-4	6.7389-4	1.0731-1	5.6820-1	1.3962-2	2.8781-2	1.0542-1	8.0092-2	5.2524-2
5	3.1007-6	1.3714-3	7.5584-3	7.9011-2	6.0274-1	3.5530-2	8.9253-3	1.0131-1	6.7123-2

TABLE 5. Franck-Condon factors to high vibrational quantum numbers for the C_2 Fox-Herzberg $B^3\Pi_g - X'^3\Pi_u$

$v' \backslash v''$	0	1	2	3	4	5	6	7	8
0	1.4369-3	1.2826-2	5.1012-2	1.2046-1	1.9023-1	2.1504-1	1.8236-1	1.2034-1	6.3754-2
1	4.9176-3	3.3567-2	9.2494-2	1.2742-1	8.1493-2	9.9149-3	1.6509-2	9.7844-2	1.6238-1
2	9.7331-3	5.1224-2	9.5733-2	6.5454-2	3.5013-3	3.0368-2	9.1015-2	6.3191-2	3.9953-3
3	1.4669-2	6.0055-2	7.3803-2	1.6848-2	1.1130-2	6.5229-2	3.9538-2	2.8033-4	5.0808-2
4	1.8718-2	6.0202-2	4.6500-2	4.6442-4	3.4636-2	4.5646-2	1.0560-3	3.4079-2	5.7214-2

$v' \backslash v''$	9	10	11	12	13
0	2.7861-2	1.0281-2	3.2669-3	9.0834-4	2.2386-4
1	1.5926-1	1.1155-1	6.0802-2	2.7111-2	1.0217-2
2	2.5140-8	1.0327-1	1.4992-1	1.3578-1	9.0583-2
3	8.1780-2	3.0748-2	8.0493-4	4.9589-2	1.1695-1
4	8.2749-3	1.7440-2	7.1192-2	5.6860-2	6.7070-3

TABLE 6. Franck-Condon factors to high vibrational quantum numbers for the C_2 Deslandres-D'Azambuja ($c^1\Pi_g - b^1\Pi_u$) system

$v' \backslash v''$	0	1	2	3	4	5	6	7	8
0	5.5083-1	3.0217-1	1.0619-1	3.0532-2	7.8455-3	1.8797-3	4.2980-4	9.5066-5	2.0502-5
1	3.5613-1	9.4332-2	2.6413-1	1.7509-1	7.4478-2	2.5412-2	7.6113-3	2.0945-3	5.4340-4
2	8.4095-2	3.9457-1	1.1158-4	1.5034-1	1.8469-1	1.1138-1	4.8806-2	1.7821-2	5.7893-3
3	8.6154-3	1.8062-1	3.1377-1	3.3201-2	5.8565-2	1.5371-1	1.3025-1	7.1957-2	3.1497-2
4	3.4244-4	2.6977-2	2.5951-1	2.0869-1	8.8989-2	1.0906-2	1.0660-1	1.2967-1	8.9610-2
5	2.6811-6	1.3440-3	5.3123-2	3.1208-1	1.1889-1	1.2873-1	1.8475-4	6.1353-2	1.1405-1
6	1.6219-8	1.0619-5	3.1685-3	8.4248-2	3.3965-1	5.6088-2	1.4428-1	1.1745-2	2.7417-2

TABLE 7. Franck-Condon factors to high vibrational quantum numbers for the C_2 Swan ($A^3\Pi_g - X^3\Pi_u$) system

$v' \backslash v''$	0	1	2	3	4	5	6	7	8
0	7.3521-1	2.1299-1	4.3116-2	7.3685-3	1.1290-3	1.5815-4	2.0200-5	2.2948-6	2.1734-7
1	2.3964-1	3.6359-1	2.7839-1	9.1572-2	2.1685-2	4.2612-3	7.3256-4	1.1190-4	1.5012-5
2	2.4459-2	3.6141-1	1.6196-1	2.7071-1	1.2956-1	3.9873-2	9.6382-3	1.9745-3	3.5267-4
3	6.0678-4	5.9842-2	4.1392-1	6.0271-2	2.3192-1	1.5271-1	5.8658-2	1.6942-2	4.0459-3
4	5.5115-7	2.1773-3	9.8472-2	4.2756-1	1.5311-2	1.8441-1	1.6203-1	7.5545-2	2.5514-2
5	2.1740-7	3.8862-7	4.1610-3	1.3623-1	4.2108-1	9.1898-4	1.3917-1	1.6060-1	8.9045-2
6	7.0147-11	1.2358-6	2.5079-7	6.2936-3	1.7109-1	4.0579-1	1.6223-3	1.0079-1	1.5182-1
7	1.7848-10	2.5007-10	3.9227-6	8.2977-6	8.2031-3	2.0219-1	3.8838-1	8.5489-3	7.0408-2
8	1.7883-12	1.2537-9	1.0832-8	9.0464-6	4.4554-5	9.5676-3	2.2925-1	3.7272-1	1.6832-2
9	7.9470-14	2.9973-11	4.4814-9	8.8068-8	1.6657-5	1.4280-4	1.0150-2	2.5226-1	3.6094-1
10	1.5722-14	3.0887-13	2.2908-10	1.0365-8	4.0284-7	2.5451-5	3.4883-4	9.8199-3	2.7118-1
11	9.7273-16	1.6637-13	7.7563-14	1.1066-9	1.5973-8	1.3269-6	3.2488-5	7.1409-4	8.5784-3
12	3.7499-17	6.1945-15	8.8470-13	2.8168-12	3.8682-9	1.4030-8	3.4847-6	3.3780-5	1.2845-3
13	6.4868-17	1.0561-17	7.1793-14	3.0065-12	5.3820-11	1.0471-8	2.1434-9	7.6779-6	2.6234-5

$v' \backslash v''$	9	10	11	12	13
0	1.4327-8	2.7418-10	6.1829-11	9.5247-11	4.7276-11
1	1.6850-6	1.3762-7	4.6135-9	2.1048-10	7.1365-10
2	5.4844-5	7.1041-6	7.0484-7	3.5017-8	1.3613-10
3	8.3043-4	1.4740-4	2.2083-5	2.5601-6	1.7185-7
4	6.9828-3	1.6239-3	3.2521-4	5.5135-5	7.3985-6
5	3.4578-2	1.0697-2	2.7859-3	6.2263-4	1.1823-4
6	9.8547-2	4.3405-2	1.5005-2	4.3333-3	1.0711-3
7	1.3872-1	1.0408-1	5.1409-2	1.9666-2	6.2441-3
8	4.7539-2	1.2363-1	1.0609-1	5.8187-2	2.4423-2
9	2.3983-2	3.0999-2	1.0821-1	1.0519-1	6.3516-2
10	3.5422-1	2.8884-2	1.0451-2	9.3517-2	1.0208-1
11	2.8592-1	3.5316-1	3.1186-2	1.1656-2	8.0171-2
12	6.5773-3	2.9617-1	3.5807-1	3.0960-2	6.5757-3
13	2.0843-3	4.1424-3	3.0144-1	3.6907-1	2.8503-2

TABLE 8. *Franck-Condon factors to high vibrational quantum numbers for the C₂ Phillips (b¹Π_u - X¹Σ_g⁺) System*

$v' \backslash v''$	0	1	2	3	4	5
0	4.1236-1	3.9817-1	1.5473-1	3.1090-2	3.4503-3	2.0875-4
1	3.3170-1	5.6587-3	2.8886-1	2.7069-1	8.8395-2	1.3623-2
2	1.6205-1	1.7295-1	5.7501-2	1.1534-1	3.0149-1	1.5525-1
3	6.2841-2	2.0003-1	3.2573-2	1.4270-1	1.7246-2	2.6322-1
4	2.1419-2	1.2505-1	1.3937-1	1.0154-3	1.5715-1	2.5365-3
5	6.7559-3	5.9704-2	1.4573-1	5.9413-2	3.5622-2	1.5915-1
6	2.0320-3	2.4250-2	9.5558-2	1.2165-1	9.7757-3	8.0346-2
7	5.9395-4	8.9460-3	4.9267-2	1.1252-1	7.5289-2	1.2709-3
8	1.7089-4	3.1039-3	2.1997-2	7.3567-2	1.0548-1	3.1284-2

TABLE 9. *Franck-Condon factors to high vibrational quantum numbers for the C₂ Balik-Ramsay (A³Σ_g⁻ - X³Π_u) system*

$v' \backslash v''$	0	1	2	3	4	5	6	7	8
0	6.3264-1	3.0651-1	5.5850-2	4.8034-3	2.0018-4	3.6882-6	2.2459-8	1.3197-11	2.6323-14
1	2.7082-1	1.8572-1	3.9354-1	1.3231-1	1.6697-2	9.1714-4	2.0873-5	1.4930-7	9.2627-11
2	7.4773-2	2.9573-1	2.2032-2	3.6188-1	2.0686-1	3.6164-2	2.5187-3	6.8891-5	5.6689-7
3	1.7212-2	1.4558-1	2.2056-1	4.0121-3	2.7815-1	2.6652-1	6.2457-2	5.3743-3	1.7319-4
4	3.6280-3	4.8567-2	1.8220-1	1.2646-1	4.6055-2	1.8372-1	3.0517-1	9.4055-2	9.8190-3

$v' \backslash v''$	9	10	11	12	13
0	1.1545-16	2.0194-18	1.4300-16	9.3339-17	6.8311-18
1	2.7707-13	1.8307-16	4.8804-17	1.1030-16	4.1606-16
2	3.6613-10	1.3992-12	4.2312-15	1.0989-16	6.1078-17
3	1.6139-6	1.0667-9	5.3184-12	1.9904-14	5.7532-16
4	3.6727-4	3.8274-6	2.5420-9	1.5550-11	1.0865-13

The Morse model for potentials implies that $\omega_e y_e$ is zero. Ballik and Ramsay [1963b] report very small $\omega_e y_e$ values for most states. For only two cases is $\omega_e y_e$ greater than unity: c¹Π_g (-4.02) and B³Π_g (2.805). For both of these v_{\max} is low enough that the divergence from Morse behavior is small. Some comments were made in the preceding paper of this series [Nicholls 1965] on the relative unimportance of the adequacy of the model of potential used when the Franck-Condon factors are used twice compensatingly as a smoothing parameter in the determination of transition probability parameters from band intensity measurements.

Most of the data of this paper was presented orally at the AGARD Combustion and Propulsion symposium in London, April 1963. Only the Franck-Condon factor surface for the C₂ Swan bands was incorporated in the proceedings of the meeting [Nicholls 1964c].

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