

Effects of rotational quantum numbers on Franck-Condon factors for molecules of astrophysical interest

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The minima r_0 of potential energy curves of a vibrating-rotating diatomic molecule have been calculated for rotational quantum number J , based on the Morse-Pekeris model with slight modifications of Shumaker (1969). Using the values of the minima of the two electronic states, it is predicted that vibration-rotation interaction on Franck-Condon factor is significant for CaH (D-X), N_2 (b-x), BH (A-X), N_2^+ (Janin-d Incan), O_2 (Herzberg 1) and is important at higher values of J for CaH (A-X), AlO (A-X), CO (fourth positive), N_2 (Vegard-Kaplan), BO (A-X), C_2 (Fox-Herzberg) band systems.

1. INTRODUCTION

The relative intensities of the individual lines in the vibrational-rotational bands of 2-atom molecules are controlled by the Franck-Condon (FC) factor

$$q_{v''J''}^{v'J'} = \left| \langle \Psi'_{v'J'} | \Psi''_{v''J''} \rangle \right|^2$$

where v' and v'' are the vibrational quantum numbers of the upper and lower electronic states. Ψ_{vJ} , the vibrational-rotational wavefunction characterising the (v,J) state is given by the Morse-Pekeris (1934) model with slight modifications of Shumaker (1969).

It is the common practice to ignore vibration-rotation interaction (VRI) effect in the calculation of FC factors (Herzberg 1950). Learner and Gaydon (1959) were the first to show that the minima of the potential energy curves of OH are displaced to larger internuclear distance and hence the modification of overlap integrals. The dependence of FC factors on the rotational quantum number J has also been studied by Learner (1962), Jain and Sahni (1966), Villarejo (1968), Villarejo *et al* (1969), Generosa and Harris (1970),

Chakraborty *et al* (1971), Chakraborty and Pan (1972) and is shown to be significant for some band systems and insignificant for some others. By a simple method, the significance of the rotational dependence on FC factors for some of the band system has been predicted here as it has important consequences for the determination of rotational temperature.

2. PROCEDURE

The effective potential for a vibrating-rotator is given by $U(r,J) = V(r) + J(J+1) \frac{h^2}{2 \mu r^2}$, where $V(r)$ is the rotationless potential, the Dirac's h , μ the reduced mass for the molecules and r is the internuclear separation. This effective potential has a minimum given by

$$r_0 = r_e [1 + 4B_e^2 J(J+1)/\omega_e^2]$$

where r_e , B_e and ω_e are the usual spectroscopic constants. This is more nearly the equilibrium internuclear distance for the rotating molecule. Thus a principal effect of VRI is the displacement of the radial coordinate with increasing J (Villarejo *et al* 1969). Hence using the values of the minima of the two electronic states, a simple method of determining an index of the influence of VRI on FC factors in the electronic spectra of 2-atom molecules has been reported by Murthy and Gowda (1976) and Gowda and Murthy (1976) and this procedure has been followed here. The FC factor depends on $\Delta r_e (= r'_e \sim r''_e)$ the separation between the minima of the potential energy curves for the two participating electronic states according to Tawde *et al* (1957) and Tawde and Murthy (1957). Extending this analogy $q_{v,v'}^{v'}$ depends on $\Delta r_0 (= r'_0 \sim r''_0)$ in the case of a vibrating-rotator. Using this criterion and reported values of $q_{v,v'}^{v'}$ of various band systems, the authors have observed that larger the change in $(\Delta r_0 \sim \Delta r_e)$ value, the greater will be the influence of VRI.

3. RESULTS AND DISCUSSION

The values of r_0 for different J at intervals of 5 from 0 to 100 have been calculated taking the molecular constants from Herzberg (1950) and Rosen (1970). The results of r_0' , r_0'' and $(\Delta r_0 \sim \Delta r_e)$ for a particular J are entered in the table along with the values of Δr_e .

From the table it can be seen that C_2 Deslandres-Azambuja, LaO (B-X), N_2^+ second negative, ZrO- α , SrO (A-X) TiO- γ and CO third positive band systems have low values of $(\Delta r_0 \sim \Delta r_e)$ even at $J = 100$. For these systems, it is predicted that the FC factors are not affected significantly with increase of J . In these cases, tedious calculations of FC factors taking into account of VRI need not be undertaken. The effect of VRI on

Table 1. Molecular constants r'_0 , r''_0 , Δr_e and $(\Delta r_0 \sim \Delta r_e) \times 10^{-8} \text{ \AA}$

| Band system | J | r'_0 in \AA | r''_0 in \AA | Δr_e in \AA | $(\Delta r_0 \sim \Delta r_e) \times 10^{-8} \text{ \AA}$ |
|----------------------------------|-----|-------------------------|--------------------------|-------------------------------|---|
| C_2 Deslandres-Azambuja | 0 | | | 0.0632 | 4.5 |
| | 100 | 1.3045 | 1.3722 | | |
| BO (B-A) | 0 | | | 0.0471 | 5.2 |
| | 100 | 1.3792 | 1.4211 | | |
| LaO (B-X) | 0 | | | 0.0300 | 2.3 |
| | 100 | 1.8713 | 1.8389 | | |
| N_2^+ Second negative | 0 | | | 0.1460 | 8.2 |
| | 100 | 1.2884 | 1.1505 | | |
| ZrO- α | 0 | | | 0.0470 | 0.2 |
| | 100 | 1.1805 | 1.7585 | | |
| SrO (A-X) | 0 | | | 0.1071 | 0.9 |
| | 100 | 2.0468 | 1.9406 | | |
| TiO- γ | 0 | | | 0.0440 | 4.3 |
| | 100 | 1.6868 | 1.6385 | | |
| CO third positive | 0 | | | 0.0928 | 8.8 |
| | 100 | 1.1500 | 1.2516 | | |
| CaH (A-X) | 0 | | | 0.0120 | 24.9 |
| | 100 | 2.8422 | 2.8791 | | |
| AlO (A-X) | 0 | | | 0.0492 | 19.2 |
| | 100 | 1.6995 | 1.6311 | | |
| CO fourth positive | 0 | | | 0.1073 | 20.3 |
| | 100 | 1.2920 | 1.1644 | | |
| N_2 Vegard-Kaplan | 0 | | | 0.1889 | 19.7 |
| | 100 | 1.3382 | 1.1295 | | |
| BO (A-X) | 0 | | | 0.1481 | 25.2 |
| | 100 | 1.4211 | 1.2478 | | |
| C_2 Fox-Herzberg | 0 | | | 0.2231 | 19.6 |
| | 100 | 1.6070 | 1.3643 | | |

Table 1 (Contd.)

| Band system | J | r'_0 in Å | r''_0 in Å | Δr_e in Å | $(\Delta r_0 \sim \Delta r_e) \times 10^{-8}$ Å |
|---|-----|-------------|--------------|-------------------|---|
| CaH (D-X) | 0 | | | 0.6080 | 60.7 |
| | 100 | 2.6917 | 2.1444 | | |
| N ₂ (b-X) | 0 | | | 0.1323 | 57.2 |
| | 50 | 1.2952 | 1.1057 | | |
| BH (A-X) | 0 | | | 0.0130 | 47 |
| | 50 | 1.5952 | 1.5612 | | |
| N ₂ ⁺ Janin-d Incan | 0 | | | 0.2970 | 50 |
| | 100 | 1.5603 | 1.2137 | | |
| O ₂ Herzberg I | 0 | | | 0.2126 | 33.7 |
| | 100 | 1.4945 | 1.2482 | | |

FC factors is important at higher values of J for CaH (A-X), AlO (A-X), CO fourth positive, N₂ Vegard-Kaplan, BO (A-X) and C₂ Fox-Herzberg band systems. The value of $(\Delta r_0 \sim \Delta r_e)$ are large for CaH (D-X), N₂ (b-X), BH (A-X), N₂⁺ Janin-d Incan and O₂ Herzberg I band system when compared to that of OH according to Gowda and Murthy (1976). In these cases a large variation in the FC factors with increase of J reflecting the influence of vibration-rotation interaction may be predicted.

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REFERENCES

- Chakraborty, B., Pan, Y. K. & Chang, T. Y 1971 J. Chem. Phys. **55**, 5147-.
- Chakraborty, B. & Pan, Y. K. 1972 J. Chem. Phys. **56**, 3722.
- Generosa, J. I. & Harris, R. A. 1970 J. Chem. Phys. **53**, 3147.
- Gowda, L. S. & Murthy, N. S. 1976 Indian J. Pure Appl. Phys. **14**, 238.
- Herzberg, G. 1950 *Spectra of Diatomic Molecules* (New York : D Van Nostrand Co.).
- Jain D. C. & Sahni, R. C. 1966 Proc. Phys. Soc. **88**, 495.
- Learner, R. C. M. & Gaydon, A. G. 1959, Nature **183**, 242.
- Learned, R. C. M. 1962 Proc. Roy. Soc. (London) **A269**, 311.
- Murthy, N. S. & Gowda, L. S. 1976 Curr. Sci. **45**, 448.
- Fekeris, C. L. 1934 Phys. Rev. **45**, 98.
- Rosen, B. 1970 *Spectroscopic data relative to diatomic Molecules* (Oxford : Pergamon Press).
- Shumaker, J. B. 1969 J. Quant. Spectrosc. Radiat. Transfer. **9**, 153.
- Tawde, N. R., Patil, B. S., Murthy, N. S. & Katti, M. R. 1957 Physica **23**, 154.
- Tawde, N. R. & Murthy, N. S. 1957 Indian J. Phys. **31**, 391.
- Villarejo, D. 1968 J. Chem. Phys. **49**, 2523.
- Villarejo, D. Stockbauer, R. & Inghram, M. G. 1969 J. Chem. Phys. **50**, 1754.