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FRANCK-CONDON FACTORS FOR THE ELECTRONIC BANDS OF THE SECOND NEGATIVE SYSTEM OF O_2^+

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ABSTRACT

The Franck-Condon factors for the second negative system of O_2^+ is recalculated by the method suggested by T. Y. Wu. For the case of Morse Oscillators, an approximate method is suggested and tested by calculating the Franck-Condon factor for the (0, 0) band of the second negative system of $^{16}O_2$.

IN many problems, it is necessary to have a theoretical knowledge of the relative band strengths for the various bands in a band system for the estimation of the temperature of the emitting gas (Stellar atmosphere, aurora night sky) from the relative intensities of the bands of a molecule. These are usually approximated by Franck-Condon factors $q_{v',v''}$, the squares of the overlap integrals of the vibrational wavefunctions $\psi_{v'}$

and $\psi_{v''}$ of the upper and lower electronic states respectively,

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

Equation (1) neglects a number of factors, including the dependence of the electronic transition moment on the internuclear separation r and rotation vibration interaction¹.

For the evaluation of Franck-Condon factors, various approximate methods have been suggested^{2,3}. Ta-You Wu⁴ suggested a method that enables the overlap integrals to be evaluated semi-analytically and applied to the calculation of the Franck-Condon factors of the bands of second negative system of O_2^+ . It can be easily seen from his results that the vibration sum rule⁵ is not satisfied. Therefore, it is considered worthwhile to recalculate the Franck-Condon factors of the bands of the second negative system of $^{16}O_2^+$ using the latest constants of Bhale and Narasimham⁶. The results of the present calculation are compared with those of T. Y. Wu as shown in Table I.

TABLE I

Franck-Condon factors of the bands of the second negative system of O_2^+

v'/v''	0	1	2	3	4	5
0 a	0.000	0.000	0.000	0.001	0.005	0.015
b	0.000	0.006	0.450	2.210	8.020	87.500
1 a	0.000	0.000	0.001	1/2.006	0.020	0.047
b	0.003	0.390	2.490	9.800
2 a	0.000	0.001	0.004	0.017	0.042	0.073
b	0.120	2.270	7.300
3 a	0.000	0.002	0.010	0.031	0.061	0.074
b	0.350	3.450
4 a	0.000	0.004	0.017	0.045	0.066	0.050
b	0.810	6.960
5 a	0.001	0.007	0.026	0.054	0.056	0.021
b	1.630	12.00

(a) $q_{v',v''}$ by the method suggested by the T.Y. Wu of present calculation, (b) $q_{v',v''}$ from the results of T. Y. Wu.

For many diatomic molecules, it is convenient and sufficient to represent the potential of a given electronic state by a Morse function. Using this Morse potential function⁷ and the vibrational wavefunction⁸ for the level v , the overlap integral $I_{v',v''}$ can be expressed as

$$I_{v',v''} = (-1)^{v'+v''} \frac{N_{v'} N_{v''}}{a} \xi^{(k''-1)/2} \sum_{l=0}^{v'} \sum_{m=0}^{v''} (-1)^{l+m} B_l B_m I_{lm} \quad (2)$$

following the approach of Wu⁴.

Where

$$B_l = {}_{v'}C_l (B' + v')_l, B_m = {}_{v''}C_m (B'' + v'')_m$$

$$(\delta)_l = \delta(\delta-1)\dots(\delta-l+1), (\delta)_0 = 1$$

$${}_{v'}C_l = \frac{v'!}{(v'-l)!l!}$$

$${}_{v''}C_m = \frac{v''!}{(v''-m)!m!} \xi^m \quad (3)$$

$$I_{lm} = \int_0^\infty \exp[-\frac{1}{2}(Z + \xi Z^\gamma)] \quad (4)$$

$$P = \frac{1}{2}(k' + rk'') - 1 - \frac{1}{2}(1 + \gamma) - l - m\gamma \quad (5)$$

For α' is not equal to α'' , the integral I_{lm} cannot be evaluated directly and therefore various substitutions have been tried to simplify the integral.

Let $z/2 = y$, $dz = 2dy$ and $k = \xi 2^{\gamma-1}$

Then I_{lm} can be transformed into

$$I_{lm} = 2^{p+1} \int_0^1 e^{-(y+k\gamma)} y^{p+1} dy \quad (6)$$

By expanding $e^{-k\gamma}$ and integrating⁹

$$I_{lm} = 2^{p+1} \Gamma(p+1) \sum_{r=0}^{\infty} \frac{(-k)^r \Gamma(p+r\gamma+1)}{\Gamma(p+1) \Gamma(r+1)} \quad (7)$$

For $\Delta\alpha$ close to 1, the above equation can be approximated as

$$I_{lm} = 2^{p+1} \Gamma(p+1) F(p+1, 1, 1, -k) \quad (8)$$

where $F(p+1, 1, 1, -k)$ is the hypergeometric function.

The correctness of the above expression can be tested for $\alpha' = \alpha''$ for which eq. (4) becomes

$$I_{lm} = \frac{2^{p+1} \Gamma(p+1)}{(\xi+1)^{p+1}} \quad (9)$$

For $\alpha' = \alpha''$, eq. (8) transforms into

$$I_{lm} = 2^{p+1} \Gamma(p+1) F(p+1, 1, 1, -\xi) \quad (10)$$

For $\xi < 1$, the hypergeometric function in eq. (10) can be easily shown¹⁰ to be $(\xi+1)^{-(p+1)}$. Therefore

$$I_{lm} = \frac{2^{p+1} \Gamma(p+1)}{(\xi+1)^{p+1}}$$

which is equivalent to eq. (9) implying the correctness of the procedure. Substitution of eq. (8) in to eq. (2) yields,

$$I_{v',v''} = (-1)^{v'+v''} \frac{N_{v'} N_{v''}}{a} \xi^{(k''-1)/2} \sum_{l=0}^{v'} \sum_{m=0}^{v''} (-1)^{l+m} B_l B_m 2^{p+1} \Gamma(p+1) F(p+1, 1, 1, -k)$$

from which Franck-Condon factors are calculated. For still higher accuracy, one has to use the eq. (7).

The method is applied for calculating the Franck-Condon factor (0.1×10^{-6}) for the (0, 0) band of second negative system of $^{16}O_2^+$. This negligibly small Franck-Condon factor obtained for the (0, 0) band is in harmony with the factor that the band is not experimentally observed.

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ADSORPTION FROM *n*-HEXANE-BENZENE MIXTURES

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ABSTRACT

Two samples of tin oxide, in the form of gel and precipitate have been prepared. Their surface properties like surface area, pore structure and surface acidity have been studied. Adsorption from *n*-hexane-benzene mixtures on these oxides reveals that *n*-hexane is preferentially adsorbed. This is explained in terms of low density of polar sites on the surface responsible for the adsorption of benzene molecule. It is observed that the surface of the tin oxide precipitate is more polar than the gel. In the case of tin oxide gel the porosity is also contributing to the preferential adsorption of *n*-hexane. Isotherms of concentration change are analysed by Schay-Nagy and Everett methods to yield the amounts of individual components in the adsorbed phase.

INTRODUCTION

ADSORPTION from binary solutions of non-electrolytes has been used to characterise the nature of the surface including polarity, distribution and density of active sites and heterogeneity of the surface¹⁻⁵. *n*-hexane-benzene is an interesting mixture for such investigations in view of the comparable areas but different geometrical disposition of the components. Kiselov and Pavlova⁶, from their adsorption studies on Linde molecular sieve 5A, using this liquid mixture, observed that *n*-hexane was completely taken up by the solid and benzene was excluded. They explained their result by assuming that the openings of the pores in Linde molecular sieve 5A were too small to admit molecules of benzene, but molecules of *n*-hexane were admitted in the vertical position. Zhdanov *et al.*⁷ studied the adsorption of *n*-hexane-benzene mixtures on the zeolites and found that the interaction between the π electrons of the benzene ring and the ionic lattice of the zeolite was so strong that *n*-hexane was completely excluded over virtually the whole range of concentration. Exhaustive

investigations on a variety of solids is therefore necessary before we can know the circumstances favouring the adsorption of these components on the surface. The adsorption of *n*-hexane-benzene on tin oxide in the form of gel and precipitate is presented in this paper with a view to studying the influence of the structure of the adsorbent on the nature of adsorption. A study of this oxide system is of particular interest as the oxide is a semi-conductor⁸ and an active catalyst for the oxidation of hydrocarbons⁹.

MATERIALS AND METHODS

Tin Oxide Gel.—Equal volumes of 1.2 N ammonium hydroxide and 1.0 N stannic chloride solutions were mixed by vigorous shaking and the gel formed was allowed to settle overnight. The gel was washed several times with distilled water and then dried at 30° C and finally crushed to pass through a 100 mesh sieve.

Tin Oxide ppt.—Stannic oxide was prepared by the action of tin on con. nitric acid. The oxide was washed with distilled water to make it free from nitrate ions. It was dried at 120° C.

Surface Area and Pore Structure

Surface area of the samples was determined by adsorption of nitrogen at -183° C using a volumetric apparatus. Pore structure was determined

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