ON THE WORKING OF SOME THEORIES OF VIBRATIONAL TRANSITION PROBABILITIES

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INTRODUCTION

The need for accurate knowledge of vibrational transition probabilities in electronic band spectra of diatomic molecules has been felt by many a worker in the field of Astrophysics and by those engaged in elaborating on fundamental concepts of mechanism causing the intensity of emitted radiation from diatomic oscillators. In view of the earlier findings of some authors that experimental results for the same system differed appreciably from one excitation condition to the other and that different theoretical procedures resulted in giving differing values, the problem of transition probabilities needs close scrutiny from both theoretical and experimental aspects. Under theoretical formulations, the relative efficacy of the methods can be judged only by studying them in comparison with carefully determined experimental data in a system or systems. The present investigation aims at testing the relative merits of a few among them, viz. (*a*) Hutchisson's method (1930) based upon relatively simpler concepts of harmonic oscillator, and (*b*) Gaydon and Pearse's method (1939), in order to see how far the latter fulfils the predictions about anharmonicity sought to be introduced by the process of distortion of harmonic wave-functions.

For the purposes of the above problems, Swan bands of C_2 molecule have been chosen for the following reasons: (i) Though the theoretical transition probabilities on this system by Hutchisson's method are available from computations given by some earlier workers, some of the results are found to differ from each other and hence fresh calculations were called for to examine the discrepancies; (ii) further, at the time this investigation was undertaken, the corrections for anharmonicity on this system in transition probability calculations were not available by any of the known methods and hence the use here of the method of numerical integration suggested by Gaydon and Pearse (1939); (iii) there is large accumulation of experimental data on this system which are either inconsistent among themselves or have not been utilised for the purpose of theoretical study. This led the present authors to attempt fresh experimental and theoretical study, which at the same time was directed towards the problems of combustion phenomena in another independent scheme of investigations.

THEORETICAL COMPUTATIONS

(*a*) Hutchisson's method.

The transition probabilities being dependent upon the square of the overlap integral $\int \psi_{v'} \psi_{v''} \, dr$, Hutchisson (1930) has, on assumptions of linear oscillations, developed an expression for it in terms of ν_0, the vibrational frequency; Δr the

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difference in the internuclear distance in the two states and μ the reduced mass of the molecule. With the following constants of vibrational frequencies adopted from latest work of Philips (1948).

$$\nu_0' = 1788 \cdot 22 \text{ cm.}^{-1}$$
$$\nu_0'' = 1641 \cdot 35 \text{ cm.}^{-1}$$

and $\triangle r = 0 \cdot 046$ A.U. close to the value $0 \cdot 0457$ of the same author, the vibrational transition probabilities for some bands of C_2 (Swan) system were calculated by the use of Hutchisson's intensity integral. These values are given below along with the earlier available results. The values of Wurm (1932) are not included as they have been already shown in serious error by McKellar and Buscombe (1948).

TABLE 1

Band	Computed transition probabilities from Hutchisson's expression.		
	Tawde and Patel (1950)	McKellar and Buscombe (as corrected) by McKellar and Tawde 1951)	Present Authors
0,0	$0 \cdot 72_6$	$0 \cdot 71$	$0 \cdot 73$
0,1	$0 \cdot 24$	$0 \cdot 25$	$0 \cdot 24$
0,2	$0 \cdot 03$	$0 \cdot 03$	$0 \cdot 03$
1,0	$0 \cdot 22_5$	$0 \cdot 23$	$0 \cdot 23$
1,1	$0 \cdot 33_7$	$0 \cdot 31$	$0 \cdot 33$
1,2	$0 \cdot 36$	$0 \cdot 36_7$	$0 \cdot 36$
1,3	$0 \cdot 07_6$	$0 \cdot 08_7$	$0 \cdot 08$
2,0	$0 \cdot 04_5$	$0 \cdot 04_8$	$0 \cdot 04$
2,1	$0 \cdot 30$	$0 \cdot 30_6$	$0 \cdot 30$
2,2	$0 \cdot 12$	$0 \cdot 10$	$0 \cdot 12$
2,3	$0 \cdot 39$	$0 \cdot 39$	$0 \cdot 39$
2,4	$0 \cdot 13_7$	$0 \cdot 14_7$	$0 \cdot 14$

It will be seen that all the above computations are close to each other, the disparities being attributable to small differences in constants used.

(b) Method of numerical integration

Owing to many practical difficulties in the evaluation of overlap integral for anharmonic oscillations by analytical methods, involving the use of more complicated mathematical expressions, such as, the one given later by Hutchisson (1931), Gaydon and Pearse (1939) suggested the method of numerical integration in which wave-functions corresponding to the harmonic oscillator are distorted to fit the Morse expression. By this method overlap integrals have been calculated and converted to squares in order to arrive at numbers proportional to transition probabilities. They have been entered in Table 2. As these calculations were completed and incorporated in a thesis, similar independent study of C_2 Swan bands by this method was reported by Pillow (1951). This enabled us to check the correctness of our procedures and at the same time our results appeared to be complementary to that work from the point of view of more comprehensive and consistent

experimental data included in them for comparative aspects of theoretical study, especially of the procedures outlined by Pillow (1951).

EXPERIMENTAL DERIVATIONS

The theoretical results are examined against the background of experimental data available from 4 independent observers: (a) present authors' study of C_2 (Swan) bands in 4 types of ethyl-alcohol flames, (Laud, 1951) forming a part of systematic spectroscopic study of combustion in flames under communication elsewhere; (b) Tawde and Patel's study (1937) in 5 types of oxy-coal gas flames; (c) Patel's (1947) results in 4 different flames and (d) King's (1948) intensity study of Swan bands in furnace. These experimental results are given side by side with all theoretical computations including those of Pillow (1951, 1953) from her original and improved methods in Table 2.

DISCUSSION

It will be seen first of all that our own computed values (column 3 above) from the unmodified distortion process nearly agree with Pillow's values (column 4) except in 3 bands. The few deviations seen are likely to be slips in calculations or may be due to the smaller or larger magnitudes of dr intervals in the numerical integration or both. In general, the two independent calculations by the same integration procedure appear to be quite in keeping with each other and thus the two sets of values can be taken to be quite representative of the method.

The analytical and numerical methods reveal quite a large departure in the resulting values, which cannot be said to be even approximately close. The question therefore is, which of the two sets of theoretical values can be taken as standard for the purposes of experimental verification.

Since the method of numerical integration attempts to take anharmonicity into account by distorting the wave-functions of harmonic oscillator to fit the Morse expression, one should expect fair agreement between the two theories for values of lower quanta. However, this is not the case, and we have therefore to examine the relative efficacy of each of these theories independently by reference to experimental values.

It is rather surprising to note that in spite of the approximate nature of Hutchisson's theory (1930), i.e. its limitations to harmonicity, the weight of agreement is more in favour of it than the method of numerical integration. Further, the general manner of approach of the two theories to experimental results is in contrast with each other, for in a good number of bands, the results of one theory are lower, and of the other, higher than the experimental values.

Whatever has been found as small disagreement with Hutchisson's theory, appears to be systematic, inasmuch as, the experimental values of bands on $r_{max} \rightarrow r_{max}$ side, are higher than the theoretical ones and reverse is the case for bands on $r_{min} \rightarrow r_{min}$ side. If, therefore, any modification is to be made in Hutchisson's theory to bring it in accord with experimental values, it must be to correct for the above dispersions in the right directions and by right magnitudes. Such corrections are possible to be introduced in the theoretical values by using experimentally justified Morse potential energy function. This is equivalent to introduction of anharmonicity which is not inherent in the basic assumptions of Hutchisson's theory.

The method of numerical integration is supposed to take anharmonicity into account through the process of distortion of Hermitian polynomials to fit the Morse expression. But it appears from the great disparity in results shown by the method that anharmonicity sought to be introduced by it, is not only not effective, but it widens the gulf further between the theory and experiment. There is, no doubt, a tendency in the method to shift the results in the right direction, but the magnitude

TABLE 2

Band	THEORETICAL					EXPERIMENTAL				King's data	
	Analytical method of Hutchisson: (authors' computations)	Numerical Integration				Present authors' mean of 4 sets	Tawde and Patel's mean of 5 sets (1937)	Patel's mean of 4 sets (1947)	as calculated by authors.	as calculated by Pillow (1951).	
		Authors' computations: (old distortion process)	Pillow's earlier distortion process (1951)	Pillow's improved distortion process (1951)	Pillow's new method (1953)						
0,0	0·73	0·84	0·83	0·77	0·73	0·69	0·61	0·54	0·78	0·67	
0,1	0·24	0·13	0·15	0·20	$0·22_6$	0·24	0·28	0·32	0·19	0·16	
0,2	0·03	0·03	0·02	0·05	0·04	0·07	0·11	0·13	0·03	0·03	
1,0	0·23	0·39	0·38	0·23	$0·23_6$	0·26	0·35	0·35	0·24	0·24	
1,1	0·33	0·40	0·40	0·38	$0·37_5$	0·33	0·28	0·23	0·35	0·35	
1,2	0·36	0·15	0·21	0·28	0·29	0·30	0·24	0·26	0·33	*0·36* (0·31)	
1,3	0·08	0·06	0·04	0·11	$0·09_7$	0·11	0·12	0·15	0·08	0·08	
2,0	0·04	0·04	0·07	0·02	$0·02_7$	0·03	0·07	0·05	0·03	0·03	
2,1	0·30	0·55	0·55	0·38	0·36	0·38	0·37	0·35	0·35	0·35	
2,2	0·12	0·19	0·23	0·18	$0·17_8$	0·14	0·13	0·12	0·17	*0·26* (0·17)	
2,3	0·39	0·14	0·24	0·25	0·28	0·32	0·26	0·23	0·33	0·33	
2,4	0·14	0·08	0·08	0·18	0·15	0·13	0·16	0·26	0·12	0·13	

N.B.—The figures in italics in the last column, as now ascertained from Pillow in a private communication, are wrong figures overlooked in proof-checking. The corrected numbers are shown in parenthesis.

of the shift appears to be too much exaggerated, so much so, that it goes beyond the required limit. It is, therefore, thought that the various approximations involved in the distortion process, departure from normalization, etc., are responsible for the large shift, much in excess of what is required to obtain the proper wave-functions, for satisfying anharmonicity.

After the above views were advanced in a thesis by one of the authors (B.B.L.), Pillow's paper (1951) mentioned above appeared, giving a refined process of distortion of harmonic wave-functions, including the corrections for normalization, thus justifying the improvements earlier visualised by (B.B.L.).

Pillow's method of distortion tested by her in the case of C_2, gives a much closer approach of the theoretical values to experiment and as such it is considered to be a great improvement over the older distortion method. Her values are recorded in column 6 of Table 2.

Pillow tested the performance of the new distortion process by the C_2 (Swan) band computations on it, with one set of experimental results of King (1948) and mean of 5 sets of results of Johnson and Tawde (1932). It may be pointed out that even though the closeness between the results of theory and experiment is good, the major portion of experimental material, i.e., five sets of values of Johnson and Tawde used for comparison by Pillow, have their limitations, because of the diverse conditions of excitation of bands (mild flame excitation to voilent spark condition), giving appreciable departures between the different sets. Under these circumstances, the comparison with Johnson and Tawde's mean set of values is not quite justified and if these results are left out of consideration, it cannot be adequate too. On the other hand, the data of experimental observations relied upon for comparative study here, is the mean of 4 sets of reasonably consistent values, resulting from slightly varying conditions of steady flame sources under controlled parameters, which were examined and found in effective temperature equilibrium of vibrational energy. With the authors' results on ethyl-alcohol flames, the data of King (1948) on furnace spectrum, Tawde and Patel's (1937) values on oxy-coal gas flames and Patel's (1947) values on different flames, the performance of Pillow's improved method of distortion, emerges much more satisfactory, than made out earlier by her with the help of experimental material having limitations indicated above.

The way in which the data of King has been used by Pillow to derive the experimental transition probabilities needs some criticism. The values given by King are proportional to transition probabilities and Pillow has explained to us in a private communication that in order to convert these to a scale resulting in her case as 0·67 for the (0, 0) band (column 11), she divided each value by 1·5, which is probably a rough average, according to her, of the sums of v''-progressions. On this basis, two of the values in her set should have been 0·31 for (1, 2) band and 0·17 for (2, 2) band, instead of 0·36 and 0·26 respectively. These, in fact, as now ascertained from Pillow, are errors overlooked in proof-checking.

Leaving apart the question of small slips mentioned above, the choice of value 1·5 for conversion appears to be arbitrary. (a) It violates the requirement that

$$\sum_{v''} \left[\int \psi_{v'} \, \psi_{v''} \, dr \right]^2 = 1,$$

assuming electronic transition moment to be constant; and (b) it ignores the question of distribution of population at various levels. The right procedure should, in our opinion, be to divide each value in a v''-progression by the sum of the progression. Pillow also seems inclined to favour it as expressed in her latest communication to us. Values thus calculated are given in Table 2. It may be noted that the calculational procedure as adopted by us, brings the experimental transition probabilities of King (column 10) much nearer to Pillow's theoretical

values (column 5), than were her own figures of transition probabilities from King's values (column 11).

Very recently Pillow (1953) has given a fresh set of values of transition probabilities of C_2 (Swan) bands, calculated as per method mentioned by her in the earlier paper (Pillow, 1951). These are included under column 6 of Table 2. It can be seen that they are, in still better agreement, with experimental values, particularly with those of King and of the present authors.

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ABSTRACT

Attempt has been made to test the relative merits of two theoretical methods of calculating transition probabilities, viz. (i) Hutchisson's method and (ii) Gaydon and Pearse's method of numerical integration. Transition probabilities C_2 (Swan) bands have been calculated by these methods and these have been studied in comparison with the carefully determined experimental data. It has been observed that in spite of the approximate nature of Hutchisson's theory, the weight of agreement is more in favour of it than the method of numerical integration. The disagreement with the latter method is attributable to the various approximations involved in the distortion process, departure from normalization, etc. The new method suggested by Pillow takes these factors into account and values calculated by this method agree with the experimental values of the present authors as well as some earlier observations on flames, thus justifying the improvements previously visualised by the authors.

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