

ON THE CALCULATIONAL PROCEDURES IN THE  
DERIVATION OF THE VIBRATIONAL TRANSI-  
TION PROBABILITIES OF THE FIRST  
NEGATIVE ( $b^4\Sigma_g^- \rightarrow a^4\Pi_u$ ) BANDS OF  $O_2^+$

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**ABSTRACT.** Recently, Rao and Ranade have published some calculations of vibrational transition probabilities of the bands of  $O_2^+$  (first negative) system. A study of that paper has revealed two very serious errors in the calculations and in the usage of the methods applied by the authors. The first error is due to the wrong usage of mathematical technique of Manneback for the calculation of vibrational transitional probabilities, and the other error is in the interpretation and derivation of transition probabilities by the application of the method of Manneback and Rahman.

Rao and Ranade (R & R) (1957) gave calculations of what, according to them, are transition moments and vibrational transition probabilities of the bands of the first negative system of  $O_2^+(b^4\Sigma_g^- \rightarrow a^4\Pi_u)$ . They have applied the methods of (i) Manneback (1951) and (ii) Manneback and Rahman (1954) to compute these values. These data have been studied by them in terms of the available values of transition probabilities of Jarman, Fraser and Nicholls (1955) on this system. As a result of this comparative study, they have emphasised the earlier conclusions of Shuler (1950, 1952) on OH ( $A \rightarrow X$ ) system, that howsoever one may take the mechanical anharmonicity of the wave function into account in any theory of vibrational transition probability, the contribution at the same time, of the variation of electronic transition moment with internuclear separation  $R$ , could not be neglected, as it is an important factor for consideration.

The application of the theory of Manneback and Rahman to such problems requires the knowledge of the exact relation of electronic transition moment with  $R$  for the particular band system. For without it, the contribution of this variation to the vibrational transition probability in relation to that of mechanical anharmonicity cannot be judged. To our knowledge, neither this relation, nor the experimental vibrational intensities for any of the bands of this system, from which this relation could be obtained, are on record. This aspect aroused our interest in the calculations of (R & R). A careful scrutiny of their paper brought out certain very fundamental points and issues which nullify their results and the conclusions based on them. It was therefore thought imperative to put these findings on record, in order to see the work of (R & R) in its proper perspective.

I

It has been shown already by Tawde, Patil, Sreedhara Murthy and Katti (1957) in the case of  $\text{OH}(A \rightarrow X)$  system that Hutchisson's and Manneback's analytical treatments, although differing in complexity, lead to exactly identical results. This test has been applied here to the first negative band system of  $\text{O}_2^+$  under consideration, employing the same constants as those used by Rao and Ranado (1957). The transition probabilities are calculated by Hutchisson's and Manneback's methods and these results are presented in Table I in columns 2 and 3. For comparison, the values of (R & R) by Manneback's method are reproduced side by side in column 4.

TABLE I  
Calculated transition probabilities.  
 $\text{O}_2^+(\text{First negative}) \quad b^a \Sigma_u \rightarrow a^a \pi_u$

Band $v', v''$	Hutchisson (present authors)	Manneback (present authors)	Manneback (R & R)
0,0	0.255	0.255	0.255
0,1	0.373	0.373	0.323
0,2	0.246	0.246	0.181
0,3	0.096	0.096	0.059
1,0	0.323	0.323	0.373
1,1	0.033	0.033	0.033
1,2	0.092	0.092	0.082
1,3	0.258	0.258	0.195
2,0	0.228	0.228	0.300
2,1	0.050	0.050	0.061
2,2	0.159	0.159	0.164
2,3	0.000 <sub>3</sub>	0.000 <sub>3</sub>	0.000 <sub>2</sub>
3,0	0.118	0.118	0.175
3,1	0.168	0.168	0.226
3,2	0.009	0.009	0.010
3,3	0.127	0.127	0.135

It is evident from the table that even in the case of this system as in  $\text{OH}(A \rightarrow X)$  system, there is complete agreement between the results emerging from both the methods, viz., Hutchisson's and Manneback's, and this is as it should be, as made out in the work of Tawde, Patil, Sreedhara Murthy and Katti (1957), and will be further shown by mathematical equivalence between the two in a forthcoming paper. The fact that the calculated values of (R & R) by the same mathematical treatment do not agree with ours indicates that they have badly erred in following the method of Manneback (1951), and applying it to the problem in hand. In arriving at this conclusion, we have applied whatever internal checks were necessary at each step of the calculations, leading to the results of columns 2 and 3 (Table I), and we have reproduced the values at every stage.

Although, the method of Hutchisson is cumbersome and requires laborious calculations over protracted period, we have, as an external check, employed it here only to be sure of the correctness of our procedures in working out the data from Manneback's method.

While attempting to locate the source of the values arrived at by Rao and Ranade it was found that they resulted from the misunderstanding on the part of the authors, of the use of the two general formulae I and II given by Manneback for the calculation of  $C(n' n'')$  matrix. These formulae contain the quantities,  $\Delta$ ,  $k$ ,  $a$  and  $b$ , and are valid for any of these values including negatives as stated by Manneback. Correct values of transition probabilities would follow by the direct use of these quantities with their proper signs in the two formulae. The values happen to be negative in the particular case of  $O_2^+$  (first negative) system, and are to be directly used with their signs in the general formulae for the evaluation of  $C(n' n'')$  matrix. The square of  $C(n' n'')$  then gives the transition probabilities. This way have resulted our data of column 3 in Table I. An alternative but simpler way suggested by Manneback when negative values of the above are encountered, is to interchange the meaning of upper and lower states, *i.e.* of  $n'$  and  $n''$ , while retaining their positive values. This simpler way has been adopted by (R & R) but in using it, they have not correctly interpreted the meaning of it, which is obviously more than mere interchange of  $n'$  and  $n''$ . (R & R) have taken the above remark of Manneback to mean merely the interchange of quantum numbers,  $n'$  and  $n''$ , without considering the real meaning of it, *viz.*, interchange also of the quantities involved in the upper and lower states along with the interchange of  $n'$  and  $n''$ . The consequence is that wrong values have emerged for  $C(n' n'')$  and hence the transition probabilities, and they are represented as such in their paper. We have also tried this alternative but simpler way with its correct meaning given above, and arrived at the values identical with those of column 3 (Table I). In following the correct use of Manneback's mathematical technique, the method of Manneback has to be understood in the context of Hutchisson's analytical treatment.

## II

In their attempt to include the contribution of variation of electronic transition moment with  $R$ , to the transition probability against the background of the above results, the authors have also erred in their fundamental approach to this question. This problem is sought to be investigated through the application of Manneback and Rahman's treatment. But, in doing so, they have made untenable assumptions. This can be understood from the following analysis

Following Shuler (1950), Manneback and Rahman start from the integral involving the wave functions of the upper and lower states :

$$|M_{n'n''}| = \int \psi_{n'}(R) M_{e'e''}(R) \psi_{n''}(R) dR \quad \dots (1)$$

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where  $M_{e'e''}(R)$ , the electronic transition moment can be taken to be constant, or a variable of  $R$ . The main object of Manneback and Rahman's treatment has been to take the latter into account in the theory, viz., the variability of electronic transition moment with  $R$ , and they considered the variation according to the linear relation of Shuler viz.,  $M_{e'e''}(R) = c(1 + \rho R)$ ,  $\rho$  being the expansion coefficient. With the introduction of this relation in equation (1), the integral  $|M_{n'n''}|$  becomes

$$|M_{n'n''}| = c \left[ \int \psi_{n'}(R) \psi_{n''}(R) dR + \rho \int \psi_{n'}(R) \psi_{n''}(R) R dR \right] \quad \dots \quad (2)$$

This expression (2) is written in the form

$$|M_{n'n''}| = c[C(n' n'') + \rho D(n' n'')] \quad \dots \quad (3)$$

where  $C(n' n'') = \int \psi_{n'}(R) \psi_{n''}(R) dR \quad \dots \quad (3a)$

and  $D(n' n'') = \int \psi_{n'}(R) \psi_{n''}(R) R dR \quad \dots \quad (3b)$

The square of the quantity  $|M_{n'n''}|$  gives the transition probability,  $p$ . The expression for  $|M_{n'n''}|$  consists therefore of two terms. The first term  $C(n' n'')$  in the bracket is the same integral as referred to in Manneback's theoretical application discussed in Section I above. The second term is the additional one brought about as a result of the electronic transition moment being considered to vary with  $R$ . It consists of two factors. (a)  $\rho$ , the expansion coefficient and (b)  $D(n' n'')$ , another integral stated above. As a close parallel to the treatment for  $C(n' n'')$  matrix, Manneback and Rahman have given the following formula for computing the  $D(n' n'')$  matrix

$$D(n' n'') = X C(n' n'') + Y n' C(n' - 1, n'') + Z n'' C(n', n'' - 1) \quad \dots \quad (4)$$

where the quantities  $X$ ,  $Y$  and  $Z$  have the meaning defined by them.  $D(n' n'')$  matrix can therefore be computed if  $C(n' n'')$  matrix is known

The quantity  $|M_{n'n''}|$  in equation (3) is therefore calculable from  $C(n' n'')$  and  $D(n' n'')$ , provided the value of  $\rho$  is known. The value of constant,  $c$ , could be eliminated by considering the relative values of transition probabilities for a pair of bands. But  $\rho$  for this particular system of  $O_2^+$  (first negative) is not known, nor have (R & R) derived any value for it. Hence  $|M_{n'n''}|$  and therefore  $p$  cannot be estimated. It is therefore not understood how (R & R) could get the values of  $|M_{n'n''}|$  and hence  $p$ . It has, however, been noticed that (R & R) have assumed  $D(n' n'')$  to be itself the "overlap integral" and have taken the square of it to be the value of  $p$  for the condition under which the electronic transition moment is supposed to vary with  $R$ . This is obviously wrong, since it involves the assumptions that  $C(n' n'') = 0$ ,  $c = 1$  and  $\rho = 1$ , which are untenable. As has been shown,

$D(n' n'')$  taken along with the factor  $\rho$  is only an additional term to  $C(n' n'')$ , to take account of the variation of electronic transition moment with  $R$  in the calculation of transition probabilities. Further, the numerical values given by (R & R) for  $D(n' n'')$  are also wrong since the values of  $C(n' n'')$  on which they depend have been shown to be erroneous.

Apart from the two fundamental defects from which the calculations of (R & R) suffer, there are some minor corrections required which are not so significant as to need a particular note. As a consequence of those defects the main results of their calculations are erroneous. Hence, the conclusions drawn by them from the comparative study of those results in terms of the values of Jarman, Fraser and Nicholls (1955) cannot sustain.

#### A C K N O W L E D G M E N T

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