SEMI-THEORETICAL METHOD OF DETERMINING LIFE-TIMES

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ABSTRACT

A semi-theoretical method to determine life-times of vibrational levels of diatomic molecules based on absolute electronic transition moments, has been applied to levels $v' = 0, 1, 2, 3$ and 4 of NO $(A^2\Sigma^+ - X^2\pi_{1/2})$ system. The method yields better results for higher vibrational level $(v' = 4)$.

INTRODUCTION

LIFE-TIMES $(\tau_{v'})$ of vibrational levels of diatomic molecules are usually determined experimentally. But as pointed out by Smith et al[1] although life-times have been measured by several experimental techniques, the values obtained are found to be different. However, $\tau_{v'}$'s are extremely important in the determination of important parameters of diatomic molecules such as oscillator strengths $(f_{v',v})$, absolute electronic transition moments $(R_e(r))$ etc. Under these circumstances, an alternative way of determining $\tau_{v'}$'s would be extremely useful. In the present work, an attempt is made at a semi-theoretical evaluation of $\tau_{v'}$'s using the expressions for the absolute R_e's. A comparison between such values and experimentally measured values is also made for NO $(A^2\Sigma^+ - X^2\pi_{1/2})$ system as a typical diatomic molecule.

PROCEDURE TO EVALUATE $\tau_{v'}$'s

The details of evaluation of $\tau_{v'}$'s are given below. The oscillator strength[2] of a band is given by the following two relations.

$$f_{v',v''} = \left(\frac{mc}{8\pi^2 e^2}\right)\left(\frac{1}{\tau_{v'}}\right)\left(\frac{G'}{G''}\right)\frac{v_{v',v''} q_{v',v''} R^2(r_{v',v''})}{\Sigma v^3_{v',v''} q_{v',v''} R^2(r_{v',v''})}, \quad (1)$$

and

$$f_{v',v''} = (8mc\pi^2/3he^2)G'v_{v',v''} R^2(r_{v',v''})q_{v',v''}, \quad (2)$$

where G' and G'' are the degeneracy factors of the upper and lower states respectively and all other parameters have the usual meaning.

In (1), R's are relative R_e's which were obtained[3] for the same system of the same molecule using the intensity data of Mohlmann et al[4]. In the evaluation of these relative R_e's, two methods were involved viz the method of regression[5] and the method of Turner et al[6]. In the present investigation, using these relative R_e's[3] the oscillator strengths were obtained for each band by

using (1). These strengths in turn were substituted in (2), the absolute R_e's were computed for each band and such computed absolute R_e's were fitted to get linear and quadratic relations[3] applicable for the band system. Using these relations[3] in the following (3), one could find $\tau_{v'}$'s for any v'-level

$$\frac{1}{\tau_{v'}} = \sum_{v''} A_{v',v''} = \sum_{v''} kd_i v^3_{v',v''} q_{v',v''} R^2_e(\bar{r}_{v',v''}) \quad (3)$$

which might not be available from any experimental work. In (3) d is the degeneracy of the lower state and k is taken to be equal to $2.106.149,957 \times 10^{-6}$.

This is the method to compute semi-theoretical $\tau_{v'}$ values. However, in the present work, we use this method only to compare experimental $\tau_{v'}$'s with the computed $\tau_{v'}$'s to test the efficacy of the present method proposed. Such computed $\tau_{v'}$'s have been presented in table 1.

RESULTS AND DISCUSSION

In order to evaluate $\tau_{v'}$'s for the levels $v' = 0, 1, 2, 3$ and 4 we have used Franck-Condon $(q_{v',v''})$ factors and r-centroids $(\bar{r}_{v',v''})$ of Spindler et al[7] and the available wavelengths for $v' = 0, 1$ and 2 from the work of Mohlmann et al[4] whereas for levels $v' = 3$ and 4, we had to calculate the wavelengths by using the method as given by Herzberg[8]. Such evaluated $\tau_{v'}$'s have been recorded in table 1 for levels $v' = 0, 1, 2, 3$ and 4. The experimental $\tau_{v'}$'s are also given for comparison. The molecular constants required in the present work are taken from Huber et al[9].

During determination of the $\tau_{v'}$'s, we have used two sets of relative $R_e(r)$ equations[3] obtained by the method of regression[5] and by the method due to Turner et al[6] and the experimental $\tau_{v'}$'s from Mohlmann et al[4] and Smith et al[1]. The experimental $\tau_{v'}$ value of Hikida et al[10] is also given in table 1. This is to compare the theoretical performance of $\tau_{v'}$ by the present semi-theoretical method. On the basis of a

Table 1 *Comparison of theoretically evaluated life-times $(\tau_{v'}$'s) with experimental ones.*

| | Experimental | | | Theoretical | | | |
| | | | | R_e with Mohlmann τ_v's | | R_e with Smith τ_v's | |
v'	Mohlmann	Smith	Hikida	Method of regression	Method of Turner-Nicholls	Method of regression	Method of Turner-Nicholls
0	200	187	—	176	189	166	178
1	195	187	—	168	170	159	161
2	190	177	—	178	169	168	159
3	—	165	—	153	127	145	120
4	—	—	118	151	112	142	105

$(\tau_{v'}$ values are to be multiplied by 10^{-9} s)

favourable comparison between theoretically evaluated transition probabilities and the integrated intensity measures, the quadratic expressions[11] were found suitable. Therefore, in the present work, only quadratic absolute R_e expressions[3] have been employed.

Looking at table 1, one could say that for $v' = 0, 1$ and 4 there is close agreement between theoretically evaluated $\tau_{v'}$'s using the method of Turner *et al*[6] (of finding absolute R_e's) and experimentally measured $\tau_{v'}$ values of Smith *et al*[1] and Hikida *et al*[10] $(v' = 4)$. Similarly for $v' = 2$ and 3, using the method of regression[5] (of finding absolute R_e's) there is good agreement between theoretically computed $\tau_{v'}$'s and the experimental $\tau_{v'}$'s of Smith *et al*[1]. Under these circumstances we cannot compare the performance of the two methods mentioned above. However, if one considers the variation of $\tau_{v'}$'s with vibrational levels, it is noticed that only under the method of Turner *et al*[6], theoretically evaluated $\tau_{v'}$'s decrease in magnitude as v' increases. This is understandable on the basis of the Boltzmann factor exp $(- E/KT)$. This decreasing order also agrees with the variation of experimental values. Thus, we could infer that the method of Turner *et al*[6] has an advantage over the other method.

In the above comparison we have used $\tau_{v'}$ values given in table 1 which involve Mohlmann's experimental $\tau_{v'}$ values in the evaluation of absolute R_e's. Strangely, the theoretically predicted $\tau_{v'}$ values and the experimental ones of Smith *et al*[1] agree for $v' = 0, 1, 2$ and 3. For $v' = 4$ there is good agreement between theoretical $\tau_{v'}$ value and the experimental $\tau_{v'}$ value of Hikida *et al*[10] this is as it should be.

In general, it can be said that the experimental values of $\tau_{v'}$'s that we have chosen[1,4] agree fairly well between

themselves. $\tau_{v'}$ values computed by the present semi-theoretical method are in close agreement with the experimentally observed values[1,4,10].

In conclusion, as experimental determination of $\tau_{v'}$'s is not an easy task especially for higher vibrational levels and the semi-theoretical method proposed here has shown better performance at $v' = 4$, it may be surmised that such computations are of great value.

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