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 $\nu' = 0, 1, 2, 3$ and $4$ of NO ($A^2\Sigma^+ - X^2\Pi_{1/2}$) system. The method yields better results for higher vibrational level ($\nu' = 4$).

INTRODUCTION

Life-times ($\tau_{\nu'}$) of vibrational levels of diatomic molecules are usually determined experimentally. But as pointed out by Smith et al.\textsuperscript{1} although life-times have been measured by several experimental techniques, the values obtained are found to be different. However, $\tau_{\nu'}$'s are extremely important in the determination of important parameters of diatomic molecules such as oscillator strengths ($f_{\nu'\nu''}$), absolute electronic transition moments ($R_{\nu'\nu''}$) etc. Under these circumstances, an alternative way of determining $\tau_{\nu'}$'s would be extremely useful. In the present work, an attempt is made at a semi-theoretical evaluation of $\tau_{\nu'}$'s using the expressions for the absolute $R_{\nu'}$'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 $\tau_{\nu'}$'S

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

$$f_{\nu'\nu''} = \left( \frac{mc}{8\pi^2\varepsilon^2} \right) \left( \frac{1}{\nu_{\nu'}} \right) \left( \frac{G}{G''} \right)^{\nu_{\nu'} \cdot \nu_{\nu''}} \frac{R^2_{\nu'\nu''}}{\Sigma v_{\nu''}}$$  \hspace{1cm} (1)

and

$$f_{\nu'\nu''} = \left( 8mc\xi^2/\hbar e^2 \right) G^2 v_{\nu''} \cdot R^2_{\nu'\nu''} q_{\nu'\nu''}.$$  \hspace{1cm} (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 $R$'s which were obtained\textsuperscript{3} for the same system of the same molecule using the intensity data of Mohlmann et al.\textsuperscript{4} In the evaluation of these relative $R$'s, two methods were involved viz the method of regression\textsuperscript{5} and the method of Turner et al.\textsuperscript{6} In the present investigation, using these relative $R$'s\textsuperscript{3} the oscillator strengths were obtained for each band by using (1). These strengths in turn were substituted in (2), the absolute $R$'s were computed for each band and such computed absolute $R$'s were fitted to get linear and quadratic relations\textsuperscript{3} applicable for the band system. Using these relations\textsuperscript{3} in the following (3), one could find $\tau_{\nu'}$'s for any $\nu'$-level

$$\frac{1}{\tau_{\nu'}} = \sum_{\nu''} A_{\nu'\nu''} = \sum_{\nu''} kd_{\nu'\nu''}^3 q_{\nu'\nu''} R^2_{\nu'\nu''} (\tau_{\nu'\nu''})$$  \hspace{1cm} (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 $\tau_{\nu'}$ values. However, in the present work, we use this method only to compare experimental $\tau_{\nu'}$'s with the computed $\tau_{\nu'}$'s to test the efficacy of the present method proposed. Such computed $\tau_{\nu'}$'s have been presented in table 1.

RESULTS AND DISCUSSION

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

During determination of the $\tau_{\nu'}$'s, we have used two sets of relative $R(r)$ equations\textsuperscript{3} obtained by the method of regression\textsuperscript{5} and by the method due to Turner et al.\textsuperscript{6} and the experimental $\tau_{\nu'}$'s from Mohlmann et al.\textsuperscript{4} and Smith et al.\textsuperscript{11}. The experimental $\tau_{\nu'}$ value of Hikida et al.\textsuperscript{10} is also given in table 1. This is to compare the theoretical performance of $\tau_{\nu'}$ by the present semi-theoretical method. On the basis of a
Table 1 Comparison of theoretically evaluated life-times ($\tau_{\nu}$) with experimental ones.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>Mohlmann</th>
<th>Smith</th>
<th>Hikida</th>
<th>$R_e$ with Mohlmann $\tau_{\nu}$'s</th>
<th>Method of regression</th>
<th>Method of Turner-Nicholls</th>
<th>$R_e$ with Smith $\tau_{\nu}$'s</th>
<th>Method of regression</th>
<th>Method of Turner-Nicholls</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>200</td>
<td>187</td>
<td>—</td>
<td>176</td>
<td>189</td>
<td>166</td>
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<td>166</td>
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</tr>
<tr>
<td>1</td>
<td>195</td>
<td>187</td>
<td>—</td>
<td>168</td>
<td>170</td>
<td>159</td>
<td>161</td>
<td>159</td>
<td>159</td>
</tr>
<tr>
<td>2</td>
<td>190</td>
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<td>—</td>
<td>178</td>
<td>169</td>
<td>168</td>
<td>159</td>
<td>159</td>
<td>159</td>
</tr>
<tr>
<td>3</td>
<td>—</td>
<td>165</td>
<td>—</td>
<td>153</td>
<td>127</td>
<td>145</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>118</td>
<td>151</td>
<td>112</td>
<td>142</td>
<td>105</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

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

Looking at table 1, one could say that for $\nu' = 0, 1$ and 4 there is close agreement between theoretically evaluated $\tau_{\nu}$'s using the method of Turner et al (of finding absolute $R_e$'s) and experimentally measured $\tau_{\nu}$ values of Smith et al and Hikida et al ($\nu' = 4$). Similarly for $\nu' = 2$ and 3, using the method of regression (of finding absolute $R_e$'s), there is a good agreement between theoretically computed $\tau_{\nu}$'s and the experimental $\tau_{\nu}$'s of Smith et al. Under these circumstances, we cannot compare the performance of the two methods mentioned above. However, if one considers the variation of $\tau_{\nu}$'s with vibrational levels, it is noticed that only under the method of Turner et al, the theoretically evaluated $\tau_{\nu}$ decrease in magnitude as $\nu'$ 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 has an advantage over the other method.

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

In general, it can be said that the experimental values of $\tau_{\nu}$ that we have chosen agree fairly well between themselves. $\tau_{\nu}$ values computed by the present semi-theoretical method are in close agreement with the experimentally observed values.

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

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