

## Vibrational Transition Probabilities with an Asymptotic Expansion for the Morse Oscillator

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Using an asymptotic expansion, an equation has been derived for the calculation of matrix elements involved in the vibrational transition probabilities for a Morse oscillator. Resulting matrix elements and vibrational probabilities for the OH molecule agree well with those given by Heaps and Herzberg.

Evaluation of several matrix elements is needed in the theoretical investigation of the rotation–vibration spectra of diatomic molecules treated as Morse oscillators.

Matrix elements needed to calculate the vibrational transition probabilities for a Morse oscillator were treated previously by Heaps and Herzberg,<sup>1</sup> by Cashion<sup>2</sup> and, more recently, by Badawi *et al.*<sup>3</sup> Herman and Rubin<sup>4</sup> and Badawi *et al.*<sup>3</sup> also gave expressions for the matrix elements of a Morse–Pekeris oscillator, *i.e.*, considering the influence of the vibration–rotation interaction in the molecule.

In the present investigation we report the study of the aforementioned matrix elements using an asymptotic expansion method introduced by Chang and Karplus<sup>5</sup> and developed by Chakraborty *et al.*<sup>6</sup> and Gallas *et al.*<sup>7</sup>

### THEORY

If a diatomic molecule of reduced mass  $\mu$  is represented by a Morse oscillator, defined by the parameters  $D_e$ ,  $a$  and  $r_e$ , the corresponding wavefunctions are given by

$$\Psi_v(r) = N_v e^{-z/2} z^{b/2} L_{v+b}^b(z) \quad (1)$$

where the notation is the same as in previous papers.<sup>5–7</sup>

The probability of transition between the two vibrational states of a diatomic molecule by electric dipole radiation is proportional to the square of the matrix elements  $M_{v'v''}$  of the dipole moment

$$M_{v'v''} = \int_0^\infty \Psi_{v'} M(r) \Psi_{v''} dr \quad (2)$$

where  $r$  is the internuclear separation.

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Substituting eqn (1) into eqn (2) one easily sees that

$$M_{v',v''} = (-1)^{v'+v''} \frac{N_{v'} N_{v''}}{a} \times \sum_{\lambda=0}^{v'} \sum_{\sigma=0}^{v''} (-1)^{\lambda+\sigma} \binom{v'}{\lambda} \binom{v''}{\sigma} \frac{\Gamma(k-v')}{\Gamma(k-v'-\lambda)} \frac{\Gamma(k-v'')}{\Gamma(k-v''-\sigma)} I(\lambda, \sigma) \quad (3)$$

where

$$I(\lambda, \sigma) = \int_0^{\infty} e^{-z} z^p M[r(z)] dz \quad (4)$$

and

$$p = k - \lambda - \sigma - 2. \quad (5)$$

If  $z$  is substituted by  $pt$ , eqn (4) is reduced to

$$I(\lambda, \sigma) = p^{p+1} \int_0^{\infty} e^{pg(t)} m(t) dt \quad (6)$$

where

$$g(t) = -t + \ln t \quad (7)$$

and where  $m(t)$  is a function obtained from the dipole moment of eqn (2) by two variable substitutions  $r \rightarrow z \rightarrow t$ . Now, applying an asymptotic expansion technique,<sup>8</sup> as described before,<sup>5-7</sup> and considering only the  $p^{-1}$  terms, we have

$$I(\lambda, \sigma) = p^{p+1} e^{-p} M(\rho_0) \left( \frac{2\pi}{p} \right)^{1/2} [1 + (1/12 + \varepsilon)/p] \quad (8)$$

where

$$\varepsilon = \frac{1}{2} \frac{M^{(2)}(\rho_0)}{M(\rho_0)} + \frac{M^{(1)}(\rho_0)}{M(\rho_0)} \quad (9)$$

and

$$\rho_0 = r_e + \frac{1}{a} \ln(k/p). \quad (10)$$

To compare the present method of matrix elements calculation with that given by Heaps and Herzberg<sup>1</sup> we will consider the following dipole moments

$$M_L(r) = r - r_e \quad (11)$$

and

$$M_Q(r) = (r - r_e)^2. \quad (12)$$

Then, according to eqn (9), we get the linear and quadratic contributions, respectively,

$$M_L(\rho_0) \varepsilon_L = -\frac{1}{2a} \quad (13)$$

$$M_Q(\rho_0) \varepsilon_Q = \frac{1}{a} \left( \frac{1}{\rho_0} - \rho_0 \right). \quad (14)$$

## RESULTS AND DISCUSSION

Although the problem of calculating vibrational transition probabilities has been treated analytically by several authors,<sup>1-4</sup> numerical results are found only in Heaps and Herzberg.<sup>1</sup>

Therefore, in table 1 we compare the results of Heaps and Herzberg,<sup>1</sup> for the linear matrix elements, with those obtained using eqn (11) and (13) in the evaluation of the integral in eqn (8). The matrix elements have already been divided by  $r_e$ , the equilibrium internuclear distance, in order to compare the results with those obtained by the left hand side of eqn (50) of ref. (1). The first entries are calculated using  $x_e (=k^{-1}) = 0.02527$  and the Morse constant,  $a$ , was calculated with  $a = 0.1217795 \omega_e (\mu/D_e)^{1/2}$ . The dissociation energy,  $D_e$ , was taken as  $36950 \text{ cm}^{-1}$ , i.e.,  $D_e$  was not calculated with the usual relation,  $D_e = \omega_e^2/(4\omega_e\chi_e)$ . The values of other spectroscopic constants were taken from Herzberg.<sup>9</sup> As can be seen from the table 1, the results agree extremely well.

TABLE 1.—LINEAR MATRIX ELEMENTS,  $\langle \Psi_{v'} | (r - r_e) | \Psi_{v''} \rangle r_e^{-1}$ , FOR OH<sup>a</sup>

$v'/v''$	0	1	2	3
1	0.072 01 0.071 50			
2	-0.008 298 -0.008 210	0.103 2 0.101 7		
3	0.001 581 0.001 559	-0.014 76 -0.014 49	0.128 1 0.125 3	
4	-0.000 396 -0.000 389	0.003 291 0.003 219	-0.021 45 -0.020 88	0.149 9 0.145 3
5	0.000 120 0.000 117	-0.000 935 -0.000 911	0.005 422 0.005 256	-0.028 47 -0.027 46
6	-0.000 042 -0.000 041	0.000 315 0.000 305	-0.001 712 -0.001 652	0.007 999 0.007 676
7	0.000 017 0.000 016	-0.000 121 -0.000 116	0.000 631 0.000 606	-0.002 768 -0.002 642
8	-0.000 007 -0.000 007	0.000 052 0.000 050	-0.000 263 -0.000 251	0.001 107 0.001 051

<sup>a</sup> 2nd entries have been reproduced from ref. (1).

The quadratic matrix elements (divided by the square of the equilibrium internuclear separation) were also calculated using eqn (12), (14) and (8) of the text and were found to be very similar to those of ref. (1). A difference in sign exists, because of the arbitrary nature of the sign convention. These are not reported here but are available on request.

The transition probabilities, neglecting the effect of the quadratic term, were also calculated with reference to the 1-0 transition as 100. The agreement was also found to be excellent. However, the results of ref. (1) cannot be reproduced exactly. (These values are not reported here.)

Next, in order to see the difference when compared with the experimental intensity, we calculate the ratio of  $\bar{M}_2/\bar{M}_1$  according to eqn (52) of ref. (1) using linear and quadratic matrix elements calculated by the present method. Calculated  $\bar{M}_2/\bar{M}_1$  values are 0.496, 0.647, 0.564 and 0.666, while those given by Heaps and Herzberg<sup>1</sup> are -0.483, -0.626, -0.545 and -0.639. [Negative values were obtained

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because a different sign convention was used in ref. (1) in calculating quadratic matrix elements.] The transition probabilities, including the effect of the quadratic term, were calculated considering  $\bar{M}_2/\bar{M}_1 = +0.530$  in a similar manner to ref. (1). There, the average  $\bar{M}_2/\bar{M}_1$  value had been taken as  $-0.514$ , which is the mean value of  $-0.483$  and  $-0.545$ . Our obvious choice is  $0.530$ , which is the arithmetic mean of  $0.496$  and  $0.564$ . The transition probabilities (not reported here) calculated by us do not differ much from those given by Heaps and Herzberg. Next, the intensity ratios of the 6-2, 6-1 and 7-3, 7-2 bands were recalculated from the transition probabilities. The matrix elements and the transition probabilities calculated by us give these ratios as 46.3 and 24.3, respectively, while the experimental values are 30.8 and 39.7. When the matrix elements and the transition probabilities calculated by Heaps and Herzberg are used, the ratios are found to be 44.6 and 24.4. This discrepancy between the experimental and theoretical intensity ratio have been justified in ref. (1) in view of the use of the Morse potential and the neglect of terms higher than the quadratic term. In any case, we have shown that the method described here is very reliable since it gives linear and quadratic matrix elements which agree extremely well with those of Heaps and Herzberg.<sup>1</sup> The transition probabilities, including the effect of the quadratic term, were also calculated using  $\bar{M}_2/\bar{M}_1 = 0.514$ , a value used in ref. (1). They were very different from those calculated by us using  $\bar{M}_2/\bar{M}_1 = +0.530$  and from those given by Heaps and Herzberg.<sup>1</sup> They are not reported here but the corresponding intensity ratios for the 6-2, 6-1 and 7-3, 7-2 bands were found to be 37.6 and 20.7. Thus we are in agreement with ref. (1) in finding that the transition probabilities calculated including the quadratic term are very sensitive to the choice of the value of  $\bar{M}_2/\bar{M}_1$ . The linear and the quadratic matrix elements calculated with  $a = 0.243\ 559\ (\mu\omega_e x_e)^{1/2}$  are also found to be very different from those reported by us and by Heaps and Herzberg.<sup>1</sup> However, the transition probabilities calculated relative to 1-0 transition as 100 are practically identical with those calculated with  $a = 0.121\ 779\ 5\ \omega_e(\mu/D_e)^{1/2}$ . They are not reported here but are available on request. In the present work we have not included the vibration-rotation interaction effect, which can easily be done in view of the work of Pekeris.<sup>10</sup>

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