

On the A_1/A_2 splittings in methyl bromide

DAVID L. COCHRANE and JOHN OVEREND*

Molecular Spectroscopy Laboratory, 12 Smith Hall, University of Minnesota, Minneapolis,
Minnesota 55455 U.S.A.

(Received 1 August 1984)

INTRODUCTION

As is well known, the representation carried by a vibrational combination state is given by the direct product of the representations of the substituent normal coordinates [1]. Thus, the representation of a binary combination of degenerate fundamentals in C_{3v} is $E_a \times E_b = A_1 + A_2 + E$. (In the following discussion the subscripts a and b will denote distinct degenerate fundamentals.) Since the A_1/A_2 pair, which gives rise to the parallel component of the transition, is not constrained by symmetry to remain degenerate to all orders, HERZBERG [2] predicted that vibrational anharmonicity could split the levels. Explicit expressions for this splitting were derived and discussed by GRENIER-BESSON [3] and OKA [4].

Any calculation of spectroscopic quantities to the second order requires a knowledge of harmonic frequencies, Coriolis coefficients and cubic and quartic force constants. Because of the recent analysis of methyl bromide from this laboratory [5], we are in a unique position to calculate an estimate of the magnitude of the energy difference between the A_1 and A_2 sublevels ($\Delta E_{A_1/A_2}$).

We have chosen to formulate this problem in a Cartesian representation. (For a discussion of the correspondence between polar and Cartesian formulations, see Refs [6, 7].) The generality of the analysis which leads to the expression for $\Delta E_{A_1/A_2}$ and the ease of evaluations of the appropriate matrix elements more than compensate for the less familiar viewpoint. The derivation of the appropriate matrix elements is contained in the appendix.

BENSARI-ZIZI *et al.* [8] measured the splitting of the parallel component of $\nu_4 + \nu_6$ in methyl bromide and found $\Delta E_{A_1/A_2}$ to be -3.451 cm^{-1} [8]. (It should be noted that their reported value is $\frac{1}{2}\Delta E_{A_1/A_2}$.) Using the spectroscopic constants obtained from our simple model of anharmonicity [5], we calculate a value that is within 21 % of the experimental value.

CALCULATIONS AND RESULTS

To facilitate the second order calculation, we employed the contact transformation formalism as de-

Table 1.

	$\Delta E_{A_1} (\text{cm}^{-1})$
$\nu_4 + \nu_5^*$	10.20
$\nu_4 + \nu_6$	-4.16
$\nu_5 + \nu_6$	-6.65

*A modified transformation was employed to eliminate the denominator $2\nu_5 - \nu_4$. For details of this type of correction, see Ref. [9].

veloped by NIELSEN *et al.* [9, 10]. Since we are considering the rotation-free case, the contact-transformed perturbation Hamiltonian is given by

$$H'_2 = \sum_{\substack{abcd \\ a \leq b, c \leq d}} Y_{ab}^{cd} \frac{1}{2} (q_a q_b p_c p_d + p_c p_d q_a q_b) \quad (1) \\ + \sum_{\substack{abcd \\ a \leq b \leq c \leq d}} Y_{abcd} q_a q_b q_c q_d$$

where the q s are dimensionless normal coordinates and the p s are momenta conjugate to the q s. Y_{ab}^{cd} and Y_{abcd} are reasonably complex functions of the harmonic frequencies, the Coriolis coefficients and the cubic and quartic force constants. For explicit expression for the Y s, see Ref. [10].

Because of the contact transformation, the second-order calculation is formally identical to a first-order perturbation calculation, allowing the use of zero-order harmonic oscillator wavefunctions. The various matrix elements are then easily evaluated. Our results are collected in Table 1.

CONCLUSIONS

The implications of the splitting between the A_1 and A_2 components of a binary combination are discussed in detail by BENSARI-ZIZI *et al.* [6] and will not be repeated here. As can be seen by our results, the splitting is larger than was commonly expected. We feel this effect is common to all methyl halides and that the analysis can be extended to different point groups as well.

REFERENCES

*This author was a student of Professor H. W. THOMPSON's from 1949 to 1955, and obtained a D.Phil. under his guidance.

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APPENDIX

In a symmetric-top molecule, degeneracies must be contained in a plane perpendicular to the top axis. The Cartesian representation of a degenerate fundamental can be taken to be two equivalent one-dimensional oscillators along the x and y axes. Therefore, $\{x_a, y_a\}$ can serve as a basis for the degenerate fundamental E_a while $\{x_b, y_b\}$ denotes the basis for E_b . Thus the basis for the direct product state $E_a \times E_b$ is given by

$$\begin{pmatrix} x_a \\ y_a \end{pmatrix} \times \begin{pmatrix} x_b \\ y_b \end{pmatrix} = \begin{pmatrix} x_a x_b \\ x_a y_b \\ y_a x_b \\ y_a y_b \end{pmatrix}. \quad (1A)$$

The linear combinations of the product basis corresponding to the irreducible representation of the combination state can be obtained by standard projection techniques [1]. For the particular case of C_{3v} (with the orientation such that one σ_v corresponds to the x axis) these linear combinations are given by

$$\begin{aligned} A_1 &= \frac{1}{\sqrt{2}} (x_a x_b + y_a y_b) \\ A_2 &= \frac{1}{\sqrt{2}} (x_a y_b - y_a x_b) \\ E^x &= \frac{1}{\sqrt{2}} (x_a x_b - y_a y_b) \\ E^y &= \frac{-1}{\sqrt{2}} (x_a y_b + y_a x_b). \end{aligned} \quad (2A)$$

It should be noted the degenerate species was resolved into two components which transform as x and y under the operations of C_{3v} .

The following notational convention will be employed in the following discussion:

$|x_a y_b\rangle$ will denote the combination state corresponding to one quantum of vibrational energy in the x component of E_a and y component of E_b with all other components in their zero-point states.

The Hamiltonian in the direct product basis is given by

$$\begin{array}{c|cccc} H & |x_a x_b\rangle & |x_a y_b\rangle & |y_a x_b\rangle & |y_a y_b\rangle \\ \hline \langle x_a x_b| & a_1 & a_2 & a_3 & a_4 \\ \langle x_a y_b| & b_1 & b_2 & b_3 & b_4 \\ \langle y_a x_b| & c_1 & c_2 & c_3 & c_4 \\ \langle y_a y_b| & d_1 & d_2 & d_3 & d_4 \end{array} \quad (3A)$$

with the specific form of the Hamiltonian as of yet unspecified. When $J = K = 0$, this matrix can be diagonalized by a transformation to symmetry coordinates. The transformation matrix is obtained from (2A) and given by

$$T = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 0 & -1 & -1 & 0 \end{pmatrix}. \quad (4A)$$

Therefore,

$$H' = THT \quad (5A)$$

with H' being a diagonal matrix. It immediately follows that the energy of the A_1 and A_2 components is given by

$$\begin{aligned} 2E(A_1) &= \langle x_a x_b | H | x_a x_b \rangle + \langle x_a x_b | H | y_a y_b \rangle \\ &\quad + \langle y_a y_b | H | x_a x_b \rangle + \langle y_a y_b | H | y_a y_b \rangle \\ 2E(A_2) &= \langle x_a y_b | H | x_a y_b \rangle - \langle x_a y_b | H | y_a x_b \rangle \\ &\quad - \langle y_a x_b | H | x_a y_b \rangle + \langle y_a x_b | H | y_a x_b \rangle. \end{aligned} \quad (6A)$$

By an obvious extension of the notation Eqns (6A) read

$$\begin{aligned} 2E(A_1) &= \langle x_a x_b + y_a y_b | H | x_a x_b + y_a y_b \rangle \\ 2E(A_2) &= \langle x_a y_b - y_a x_b | H | x_a y_b - y_a x_b \rangle. \end{aligned} \quad (7A)$$

Since the Hamiltonian transforms as A_1 in the point group of the problem, the calculation of the energy difference can be greatly simplified if it is noted that

$$\begin{aligned} &\langle A_1 + E^x | H | A_1 + E^x \rangle - \langle A_2 - E^y | H | A_2 - E^y \rangle \\ &= \langle A_1 | H | A_1 \rangle - \langle A_2 | H | A_2 \rangle + [2\langle E^x | H | A_1 \rangle \\ &\quad + 2\langle A_2 | H | E^y \rangle] \\ &\quad + [\langle E^x | H | E^x \rangle - \langle E^y | H | E^y \rangle]. \end{aligned} \quad (8A)$$

The first bracketed term vanishes because the representation of the matrix element does not contain the totally symmetric representation, and the second bracketed term vanishes because, in a rotation-free problem, the components of a degenerate mode are of equal energy. Therefore,

$$\begin{aligned} E(A_1) - E(A_2) &= \langle A_1 | H | A_1 \rangle - \langle A_2 | H | A_2 \rangle \\ &= \langle A_1 + E^x | H | A_1 + E^x \rangle \\ &\quad - \langle A_2 - E^y | H | A_2 - E^y \rangle. \end{aligned} \quad (9A)$$

From (2A)

$$\begin{aligned} A_1 + E^x &= \frac{2}{\sqrt{2}} x_a x_b \\ A_2 - E^y &= \frac{2}{\sqrt{2}} x_a y_b. \end{aligned} \quad (10A)$$

So Eqn (9A) becomes

$$\begin{aligned} E(A_1) - E(A_2) &= 2[\langle x_a x_b | H | x_a x_b \rangle \\ &\quad - \langle x_a y_b | H | x_a y_b \rangle]. \end{aligned} \quad (11A)$$