

## Short Communication

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### A corrected $f$ -value for the $\text{CH}_2$ ( ${}^3\text{A}_2$ - ${}^3\text{B}_1$ ) transition

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(Received October 18, 1972)

The oscillator strength for the  $\text{CH}_2$  ( $\tilde{\text{B}}\ {}^3\text{A}_2$ - $\tilde{\text{X}}\ {}^3\text{B}_1$ ) transition at 141.5 nm has been recalculated, taking into account the expected contribution from diffuse sub-bands which have been postulated in a previous reinterpretation of the  $\text{CH}_2$  spectrum<sup>4</sup>. The recalculated value is  $1.4 \times 10^{-2}$ .

#### Introduction

The electronic spectrum of methylene was first analyzed by Herzberg<sup>1</sup>, who showed that the lowest triplet state is probably linear. Pilling *et al.*<sup>2</sup> measured the oscillator strength for the  $\text{CH}_2$   ${}^3\Sigma_u^-$ - ${}^3\Sigma_g^-$  transition, occurring at 141.5 nm, obtaining a value of  $4.2 \times 10^{-3}$ . They pointed out that this is unusually small, since the transition is Rydberg in nature. Following Wasserman *et al.*'s<sup>3</sup> e.s.r. work, which indicated a bond angle of  $136^\circ$  for the lowest triplet state, Herzberg and Johns<sup>4</sup> reconsidered the assignments, and showed that the e.s.r. and optical spectra could be reconciled if the upper electronic state of the 141.5 nm band were heterogeneously predissociated. Thus instead of  $\Sigma_u^-$ - $\Sigma_g^-$ , the transition could be  $\text{A}_2$ - $\text{B}_1$ , with the  $K > 0$  sub-bands so broadened by predissociation of  $\text{A}_2$  via a  $\text{B}_2$  state, that they are lost into the background continuum and escape detection. These considerations also apply to the measurements of Pilling *et al.*<sup>2</sup>, and their quoted  $f$ -value includes only transitions from  $K'' = 0$ . It is the purpose of this note to correct this, by calculating the undetectable contribution from the  $K'' > 0$  levels.

#### Calculation

The relevant rotational constants for  $\text{CH}_2\tilde{\text{X}}\ {}^3\text{B}_1$  are given below:

$$A = 60.26 \text{ cm}^{-1}$$

$$B = 8.44 \text{ cm}^{-1}$$

$$C = 7.40 \text{ cm}^{-1}$$

These show that the molecule, although strictly an asymmetric top, has two moments of inertia which are very nearly equal, and may be treated as a prolate symmetric top. The energy levels for a rigid prolate symmetric top are given by:

$$F(J, K) = B_c J(J + 1) + (A - B_c) K^2$$

where, in this case,  $B_c$  is the mean of  $B$  and  $C$ . Since  $\text{CH}_2$  contains two equivalent atoms, we must examine the effect of nuclear spin in evaluating the overall partition function. In order to deduce the symmetries of the various  $(J, K)$  levels, we must first consider the molecule in its true ( $C_{2v}$ ) symmetry (asymmetric top) and then consider the correlation of these levels with those of a prolate symmetric top<sup>5</sup>. This leads to the conclusion that all levels of overall rovibronic species  $B$  have a nuclear statistical weight of 3, and those of species  $A$  have a nuclear statistical weight of 1. The  $K > 0$  levels are  $K$ -doubled, one level having symmetry  $A$  and the other  $B$ . Thus for  $K > 0$ , each  $J$  level has an overall statistical weight of 4 (exclusive of spin and the  $(2J + 1)$  degeneracy). The spin splitting is small, and all levels, apart from  $J = 0$ , may be considered triply-spin degenerate. Thus the overall partition function may be written:

$$Q = 3(X + Y + Z) - 6.0$$

where

$$X = \sum_{\substack{\text{even} \\ J}} 3(2J + 1) \exp \{-B'' J(J + 1)hc/kT\}$$

$$Y = \sum_{\substack{\text{odd} \\ J}} (2J + 1) \exp \{-B'' J(J + 1)hc/kT\}$$

$$Z = \sum_{K=1}^{\infty} \sum_{J=1}^{\infty} 4(2J + 1) \exp \{[-B'' J(J + 1) - (A'' - B'')K^2]hc/kT\}$$

(The subtraction of 6.0 allows for the lack of spin degeneracy in  $J = 0$ .) This leads to a value for  $Q$  of 521.4 at 300 K, and a value for  $R$  of 3.39, where  $R$  is defined by

$$R = (X + Y + Z - 6.0)/(X + Y - 6.0)$$

The intensity of an absorption line is given by

$$I_{m, \nu'', K'', J''}^{n, \nu', K', J'} = C \nu S_{K'', J''}^{K', J'} q_{\nu''}^{\nu'} |R_m^n|^2 g_{K'', J''} \exp \left[ \frac{-hcF(K'', J'')}{kT} \right],$$

where  $S_{K'', J''}^{K', J'}$  is the rotational line strength,  $q_{\nu''}^{\nu'}$  is the Franck-Condon factor,  $R_m^n$  is the electronic transition moment,  $g_{K'', J''}$  is the statistical weight of the lower level,  $\nu$  is the frequency and  $C$  is a constant. For a given band, such as the one we are considering here,  $(C \nu q_{\nu''}^{\nu'} |R_m^n|^2)$  is effectively constant. The rotational line strengths for symmetric top transitions obey the sum rule.

$$\sum_{J'} S_{K'', J''}^{K', J'} = 1, \text{ for } \Delta K = 0.$$

Thus the contribution to the overall band intensity from a given  $(K'', J'')$  level depends solely on  $g_{K'', J''} \exp [-hcF(K'', J'')/kT]$ .

The measured  $f$ -value can be corrected simply by dividing the measured value by the fraction of  $\text{CH}_2^3\text{B}_1$  molecules in the  $K'' = 0$  levels, *i.e.*

$$(\text{true } f) = (\text{measured } f) \times R$$

This leads to an  $f$ -value of  $1.4 \times 10^{-2}$ .

### Discussion

The (0,0) transition is the only band observed in the  $\text{A}_2\text{-B}_1$  system, indicating that  $q_{0,0} \sim 1.0$ . This being so, then the  $f$ -value derived above is still rather small for a Rydberg transition. In his first methylene paper, Herzberg considered the possibility of a bent ground state, and obtained approximate bond angles of  $140^\circ$  and  $126^\circ$  for the  $\text{B}_1$  and  $\text{A}_2$  states respectively. The value of  $\theta''$  obtained from e.s.r. is  $136^\circ$ , and one would expect a similar bond angle in the Rydberg states of  $\text{CH}_2$  as one finds in the ground state of  $\text{BH}_2$  ( $131^\circ$ ). Thus it seems likely that there is little change in angle on excitation of  $\text{CH}_2$  to the  $^3\text{A}_2$  state. The bond distances, however, do change significantly. Herzberg derived values of  $r'_0 = 1.162 \text{ \AA}$  and  $r_{0''} = 1.071 \text{ \AA}$ . This seems reasonable on the basis of simple molecular orbital theory. The transition probably involves excitation of the  $1b_1$  electron to a non-bonding Rydberg orbital. The energy of the  $1b_1$  orbital is unaffected by change in angle, but is lowered on decreasing the C-H bond distance. On this basis one would expect a well developed progression involving excitation of the symmetric stretching vibration in the upper state. The absence of such a progression stems, presumably, from the homogeneous predissociation which is apparent in the 141.5 nm band of  $\text{CH}_2$ , but which occurs less strongly for  $\text{CD}_2$ . Such behaviour is indicative of tunnelling, and the addition of vibrational energy to the symmetric stretching mode should lead to increased overlap of the vibronic wavefunction of  $\text{CH}_2\tilde{\text{B}}^3\text{A}_2$  with the continuum and to an enhanced rate of predissociation. This could broaden the lines to such an extent that they become lost in the background, and can no longer be observed in absorption at the concentrations used. In the absence of known vibrational frequencies for  $\text{CH}_2$  it is not feasible to calculate the Franck-Condon factors, but a value for  $q_{0,0}$  considerably less than unity seems probable.

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