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SINGLET–TRIPLET PERTURBATIONS H_2CO AND H_2CS*

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Summary

Magnetic rotation spectroscopy provides a sensitive method for probing singlet–triplet perturbations in the spectra of simple polyatomic molecules. The sensitivity of the method depends on the magnetic moment conferred by the triplet component of a mixed wavefunction and the transition moment conferred by the singlet component. High resolution magnetic rotation spectra have been obtained for the 4_0^1, 4_0^3, $2_0^1 4_0^1$, $2_0^1 4_0^3$, $2_0^2 4_0^1$, $2_0^2 4_0^3$ and $2_0^3 4_0^1$ bands of H_2CO, the 4_0^1 and 4_0^3 bands of D_2CO and the 4_0^0 and 4_0^1 bands of H_2CS. The singlet rotational levels which are perturbed by triplet levels have been identified for each of the excited vibronic states. The perturbations in the 4_0^3 band of H_2CO are particularly interesting since a complete interpretation of the quantum numbers of the perturbing triplet levels can be given; the magnitudes of the perturbing matrix elements can also be evaluated.

In the last few years at Ottawa extensive investigations have been carried out on the singlet–triplet perturbations in the near-UV bands of H_2CO [1 - 3], HDCO [4] and D_2CO [5] and current work involves the first excited singlet and triplet states of H_2CS [6].

Magnetic optical activity in the 3260 Å ($2_0^2 4_0^1$) band of formaldehyde was first reported by Kusch and Loomis [7]. The rotational analysis of this band was first carried out by Parkin [8] and many perturbations were noted. By using pulsed magnetic fields up to 13 kG, Brand and Stevens [9] found that the levels which showed the largest perturbations also showed Zeeman effects. They therefore concluded that the perturbations were produced by crossings with the levels of the $\tilde{a}\ {}^3A_2$ state. The magnetic activity of these levels was later confirmed by magnetic rotation studies [2] and, in addition, many new magnetically sensitive levels were found. Magnetic rotation spectra were obtained with much smaller flux densities (100 - 1000 G) than were needed in the Zeeman studies. The greater sensitivity of the magnetic rotation technique is connected with the fact that it operates with crossed polarizers, thus giving rise to a higher signal-to-noise ratio. Furthermore the technique has the added advantage that it selects only those lines that are magnetically sensitive.

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The magnetic rotation lines are readily identified since they lie close to corresponding absorption lines. Furthermore it is found that ${}^rR$ and ${}^pP$ lines are usually the strongest, ${}^pR$ and ${}^rP$ are weaker, while ${}^rQ$ and ${}^pQ$ lines are very weak and rarely observed. The magnetically sensitive levels in the 3260 Å band which were identified using a flux density of only 160 G are given in Table 1. A further 22 levels were identified with higher flux densities.

The theory of the mutual perturbations between the $\tilde{A}\,{}^1A_2$ and $\tilde{a}\,{}^3A_2$ states has been treated by Stevens and Brand [10]. No direct spin–orbit interaction is allowed between these two states but two mechanisms by which perturbations can occur and the corresponding selection rules are (i) the spin–orbit orbital rotation mechanism (${}^1\Gamma_e = {}^3\Gamma_e$; ${}^1\Gamma_{ev} = {}^3\Gamma_{ev}$; $\Delta J = 0$; $\Delta N = 0, \pm 1$; $\Delta K_a = 0, \pm 2$) and (ii) the vibronic spin–orbit mechanism (${}^1\Gamma_{ev} \times {}^3\Gamma_{ev} \supset R_z$; $\Delta J = 0$; $\Delta N = 0, \pm 1$; $\Delta K_a = 0$; ${}^1\Gamma_{ev} \times {}^3\Gamma_{ev} \supset R_x, R_y$; $\Delta J = 0$; $\Delta N = 0, \pm 1$; $\Delta K_a = \pm 1$). The number of perturbations in the 3260 Å ($2^2_0 4^1_0$) band is too large to be explained on the basis of a single vibrational level of the triplet state. It is clear that several vibrational levels must be involved.

The situation is much simpler in the 4^3_0 band. All the perturbations can be explained in terms of two mechanisms. The perturbations which affect the $19_{0,19}$, $19_{1,19}$, $17_{1,16}$, $17_{2,16}$, $18_{2,17}$, $16_{2,14}$, $17_{2,15}$, $17_{3,15}$, $18_{3,16}$, $17_{3,14}$ and $18_{3,15}$ levels of the excited singlet state can be explained in terms of interactions with the rotational levels of a triplet state for which $\Delta J = 0$, $\Delta N = 0$, $\Delta K_a = 0$ and $\Delta K_c = 0$. The cross-overs in the various K_a stacks at the different J values are explained without difficulty in terms of a triplet level with rotational constants very similar to those which are known for the zeroth level. The origin of the triplet level is found to be 29 125.7 cm^{-1}, with an uncertainty of a few tenths of a wavenumber. Subtracting the term value for the zeroth level, the vibrational energy of the triplet level is found to be $3931._4$ cm^{-1}. The vibrational symmetry of the triplet level can be deduced from the selection rules governing the singlet–triplet perturbations and is the same as that of the singlet level, *i.e.* b_1. Assuming that the vibrational

Magnetically sensitive levels associated with the 3260 Å band of formaldehyde

Singlet level	*Displacement* (cm^{-1})	*Singlet level*	*Displacement* (cm^{-1})
$7_{0,7}$	−0.03	$12_{4,9}$[a]	+0.038
$11_{0,11}$[a]	+0.230	$15_{4,11}$	−0.031
$18_{0,18}$	-0.02_5	$15_{4,12}$[a]	−0.029
$20_{0,20}$	−0.02	$17_{4,13}$	+0.010
$11_{2,9}$[a]	+0.061	$17_{4,14}$	+0.019
$12_{2,10}$[a]	−0.061	13_5[a]	+0.078
$12_{2,11}$[a]	−0.200	16_5	−0.018
$15_{2,14}$	+0.003	12_6	−0.005
$18_{2,16}$	+0.000	15_6	+0.045
$11_{3,8}$[a]	−0.045	16_6[a]	−0.016
$13_{3,10}$[a]	−0.110	12_7	+0.047
$13_{3,11}$[a]	−0.074	13_8	−0.06

[a] A magnetically sensitive level reported by Brand and Stevens [9].

TABLE 2

Some singlet and triplet term values associated with the 4^3 level of formaldehyde

Singlet		*Triplet*[a]		
Level	*Term value* (cm^{-1})	*Level*	*Term value* (cm^{-1})	*Difference* (cm^{-1})
$10_{2,8}$	29 283.66	$10_{3,7}$	29 283.15	+0.51
$10_{2,9}$	29 283.19	$10_{3,8}$	29 283.13	+0.06
$11_{2,9}$	29 307.30	$11_{3,8}$	29 307.33	−0.03
$11_{2,10}$	29 306.68	$11_{3,9}$	29 307.30	−0.62

[a] Calculated with $\nu_0 = 29\,094.15$ cm^{-1} and with the rotational constants for the zeroth level.

frequencies for the triplet state are similar to those for the excited singlet state, then the only reasonable assignment for the triplet level is $4^15^16^1$.

Another level (5^16^1) is expected to be about 36 cm^{-1} below the $4^15^16^1$ level and is expected to produce perturbations governed by the selection rules $\Delta J = 0$, $\Delta N = 0, \Delta K_a = \pm 1, \Delta K_c = \pm 1$. Indeed such a level readily accounts for the perturbations found in the $10_{2,8}$, $10_{2,9}$, $11_{2,9}$ and $11_{2,10}$ levels of the singlet state (Table 2). The $10_{2,9}$ and $11_{2,9}$ levels show stronger magnetic activity than the $10_{2,8}$ and $11_{2,10}$ levels and this difference in activity is explained without difficulty by the way in which the singlet and triplet levels cross. The origin of the second triplet level is 29 094.$_{15}$ cm^{-1} and lies 31.$_5$ cm^{-1} below the origin of the first triplet level.

The magnitudes of the matrix elements of the perturbations are of interest and can be deduced from the shifts associated with the perturbed levels and from the appearance of "extra" lines in the spectrum. For the $2_0^24_0^1$ band, shifts of the singlet levels up to 0.23 cm^{-1} were observed, but for the 4_0^3 band the shifts were too small to be detected by the rotational analysis of the band. Once again this emphasizes the sensitivity of magnetic rotation spectroscopy as a technique for revealing singlet–triplet perturbations.

Recently we have been studying the mutual perturbations between the corresponding $^1A_2$ and $^3A_2$ excited states of thioformaldehyde H_2CS [6]. The 4_0^0 and 4_0^1 bands of the $^1A_2$–$^1A_1$ system were investigated under high resolution both in absorption and in magnetic rotation. Perturbations were found in the 4_0^0 band for all K_a levels from 0 to 5 and the perturbed levels were found to be magnetically active, *i.e.* the perturbations are produced by triplet levels. Thioformaldehyde has the advantage that individual rotational transitions for bands of the $^1A_2$–$^1A_1$ system can be pumped with continuous-wave dye lasers using rhodamine dyes. Indeed, thioformaldehyde is one of the few polyatomic molecules for which single rotational level fluorescence has been reported [11]. Preliminary fluorescence studies have shown that the perturbed levels show marked Zeeman effects in the presence of magnetic fields of a few kilogauss while the unperturbed levels are unaffected.

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