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Sub-Doppler spectroscopy of thioformaldehyde: Excited state perturbations and evidence for rotation-induced vibrational mixing in the ground state

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High-resolution intracavity dye laser spectroscopy has been used to obtain sub-Doppler spectra of transitions to 350 rotational levels in the 4_0^1 band of the $\tilde{A} \, {}^1A_2 - \tilde{X} \, {}^1A_1$ electronic transition of thioformaldehyde. Ground state combination differences from the sub-Doppler spectra, combined with microwave and infrared data, have been used to improve the ground state rotational and centrifugal distortion constants of H₂CS. The upper state shows a remarkable number of perturbations. The largest of these are caused by nearby triplet levels, with matrix elements of $0.05-0.15 \text{ cm}^{-1}$. A particularly clear singlet-triplet avoided crossing in $K'_a = 7$ has been shown to be caused by interaction with the F_1 component of the 3^16^2 vibrational level of the $\tilde{a} \, {}^3A_2$ state. At least 53% of the S_1 levels show evidence of very small perturbations by high rovibronic levels of the ground state. The number of such perturbations is small at low J, but increases rapidly beyond J=5 such that 40%-80% of the observed S_1 levels of any given J are perturbed by ground state levels can be explained if there is extensive rotation-induced mixing of the vibrational levels in the ground state.

I. INTRODUCTION

Thioformaldehyde (H_2CS) is a transient molecule with a beautiful, sharp $S_1 - S_0$ spectrum in the 610–440 nm region.¹ Extensive spectroscopic studies²⁻¹² of the lowest vibronic transitions 0_0^0 and 4_0^1 have shown that various rotational levels of the S_1 state are perturbed by interactions with the nearby T_1 state, while others are perturbed by coupling to levels in the ground state. In particular, the $S_1 v'=0$ level shows a very pronounced singlet-triplet resonance^{2,3} that affects the $K_a = 0$ through $K_a = 5$ rotational manifolds, which is caused by interaction with the triplet state vibrational level 3¹4¹6^{1,10,12} Detailed analysis of the Doppler-limited absorption spectrum has shown that the perturbations can be guantitatively accounted for by a vibronic spin-orbit mechanism with J- and K_a -dependent matrix elements of 0.25 to 0.45 cm⁻¹. In the 4_0^1 band, by contrast, Doppler-limited magnetic rotation² (MRS) and Zeeman effect⁴ studies have shown only a few localized singlet-triplet perturbations. At sub-Doppler resolution, intermodulated fluorescence^{5,13} (IMF) and microwave-optical double resonance⁶⁻⁹ (MODR) experiments have shown that many rotational states in the 4^1 level are perturbed by nearby levels of the ground state. The perturbations are very small, with matrix elements of $10^{-2}-10^{-3}$ cm⁻¹, so that the lines appear unperturbed at Doppler-limited resolution.

Photophysical studies of the excited state decay dynamics of thioformaldehyde¹³⁻¹⁶ have lagged behind the spectroscopy. Ab initio calculations^{17,18} predict that there is no appreciable photochemical decay channel in the S_1 state. Thus, in thioformaldehyde, there is the opportunity to study internal conversion and intersystem crossing in the absence of photochemical complications. In 1990, Dunlop and Clouthier¹³ published the first photophysical study of S_1 H₂CS with single rotational level resolution under collisionfree conditions. They reported the measurement of fluorescence lifetimes and relative quantum yields of fluorescence for selected rotational states of the 4¹ vibrational level. About half the states studied were found to decay purely radiatively, with a lifetime of about 170 μ s and relative fluorescence yields of unity. The other states decayed with longer lifetimes, and these states were found to correlate with perturbations in the spectrum. Most of the perturbed levels had long lifetimes and fluorescence yields near unity, as expected in the absence of any competitive decay mechanism in the perturbing T_1 or S_0 levels. However, a few of the S_1 levels coupled to S_0 had substantially reduced relative yields of fluorescence, which was attributed to competitive infrared fluorescence from the S_0 states. A sequential coupling model was proposed which predicted that, with sufficient sensitivity and resolution, the underlying states of predominantly S_0 character should be observable, and that the number of levels should correlate with the photophysical data.

Recently, we reported¹⁹ very high sensitivity sub-Doppler intracavity dye laser experiments that directly probed the underlying structure in the spectrum for the $K'_a = 0$ and 4 rotational levels of the 4¹ vibrational level of S_1 H₂CS. It was found that perturbations due to the ground state were even more widespread than previously suspected and

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that the perturbing states could be observed as extra lines in the spectrum. The perturbations were found to correlate very well with the photophysical data: levels with reduced quantum yields of fluorescence show strong extra lines and significant level shifts, and levels with lifetimes even slightly longer than radiative usually show weak extra lines. S_1-S_0 interaction matrix elements of 0.001–0.006 cm⁻¹ were derived for cases where simple two-level perturbations were found. Some larger singlet-triplet perturbations also occur in the upper state.

In the present work, we have extended the sub-Doppler intracavity dye laser spectroscopic measurements of the 4_0^1 band in order to probe the extent and character of both the singlet-triplet and singlet-singlet interactions. Most of the observed upper state rotational levels are found to be perturbed to some extent. The spectra are complicated by collision-induced, as well as pressure-independent, crossover resonances. Extensive ground state combination differences from these measurements have been used to refine the ground state rotational constants of H₂CS. A set of selected transitions to apparently unperturbed upper state levels has been used to obtain the upper state rotational constants, which allow the determination of the energy shifts of the perturbed levels. At least 53% of the observed excited state levels are perturbed by the ground state, as indicated by extra lines or level shifts in the sub-Doppler spectra. Model calculations show that the distribution and number of perturbations can be attributed to substantial rotation-vibration mixing in the perturbing ground state levels.

II. EXPERIMENT

The experimental details have been discussed in Ref. 19. Briefly, we have constructed a high-resolution intracavity sub-Doppler spectrometer similar to that first reported by Hill and Field.²⁰ The cavity of a Coherent Inc. model 599-21 single-mode standing-wave dye laser was extended and a fluorescence cell mounted inside the cavity. A provision was made to modulate the frequency of the dye laser while scanning by applying a small sine wave voltage to the d.c. ramp voltage that drives the tipping Brewster plate. By recording the fluorescence component at twice the modulation frequency with a lock-in amplifier, second-derivative line shape sub-Doppler Lamb dip signals were obtained.

The spectra were calibrated using the wavemeter and stabilized Fabry–Perot etalon system described in Ref. 21. The absolute accuracy of the measurements is about 0.001 cm⁻¹ (30 MHz), since it represents an average over many lines of the I_2 spectrum.²² However, the precision over extended wave number regions is estimated to be about 10 MHz and the reproducibility of H₂CS measurements done months apart was found to be about 9 MHz. As a further check on the calibration, we recorded the $R_1(2)$ and ${}^{R}S_{12}(2)$ transitions in the 593 nm band of NO₂ in the intracavity apparatus. The measured wave numbers of the hyperfine lines were in excellent agreement (±5 MHz) with those obtained by molecular beam apparatus methods when the calibration system was originally constructed.²¹

Thioformaldehyde was generated by pyrolysis of trimethylene sulfide (TMS) vapor at 750 °C in a continuous flow system. By controlling the flow of TMS with a needle valve, the pressure in the fluorescence cell, as measured by a thermocouple gauge, could be maintained constant for several hours. Pressures of 10-100 mTorr were used for these experiments, depending on the intensity of the transitions being recorded.

III. RESULTS AND ANALYSIS

A. Observed spectra

In this work, we have extensively surveyed the 4_0^1 band of the $\tilde{A} {}^1A_2 - \tilde{X} {}^1A_1$ system of H₂CS at sub-Doppler resolution. This involved identifying the rotational transition of interest by rapidly scanning over the Doppler-limited line profile, then slowly scanning through the profile at sub-Doppler resolution. Each scan typically covered 2–3 GHz and took 10–20 min, depending on the time constant necessary to obtain a suitable signal-to-noise ratio. We have systematically recorded transitions from $J' = K'_a$ to J'=30 for $K'_a = 0-6$ and over a more restricted range of J' values for the weaker transitions involving $K'_a = 7-10$. A variety of typical spectra have been reported in our earlier publication,¹⁹ so we present only a summary of the experimental observations in this work.

A small fraction of the observed lines are clear examples of transitions to unperturbed upper state levels, with no evidence of extra lines or cross-over resonances within their Doppler width. More commonly, a scan over a single rovibronic transition shows more than one feature, indicating some form of perturbation in the upper state. In simple cases, the spectrum consists of a strong line, a weaker satellite line, and a line of intermediate intensity exactly halfway between the outer two lines. The central line is readily assigned as a cross-over resonance or center dip (CD), an artifact common to all saturation spectroscopic techniques. The center dip occurs when two transitions share a common level, either in the ground or excited state, and overlap within their Doppler widths. The intensity of the center dip is the geometric mean of the intensities of the individual transitions. The weaker line is an extra line resulting from direct absorption from the ground state level to a perturbing state. This interpretation was readily confirmed by recording two or more transitions with the same upper state and finding the same pressureindependent pattern of lines.

In many cases, scans over the Doppler width of a line revealed complex patterns which were not readily assignable. Often, overlapping lines were present and scans over other transitions involving the same upper state level proved invaluable in making assignments. Since the 4_0^1 band follows $\Delta K_a = \pm 1$, $\Delta J = 0$, ± 1 selection rules, in most cases there are six transitions terminating on a given upper state level, although some were too weak to be useful. By judiciously picking the appropriate transitions, complex spectra could be simplified. For example, in Fig. 1, the upper trace shows the overlapping 25_4 - 24_3 and 8_4 - 8_3 transitions, each of which is split into two lines by the effects of asymmetry. The lower two traces show other transitions also terminating on the $25_{4,22}$ level, from which it can be deduced that the $25_{4,22}$ - $24_{3,21}$ transition consists of a main line (*M*), an extra



FIG. 1. Sub-Doppler spectra showing how complex line patterns can be assigned by recording different transitions involving the same upper state level. The top trace shows the $25_{4,22}-24_{3,21}$ (*R* branch) transition overlapped by both components of the perturbed 8_4-8_3 transition (shaded lines) with associated extra lines and center dips. The middle trace shows the corresponding *P* branch transition, consisting of three lines with the same spacings as in the top trace. The 25_{4,22} level is obviously perturbed and the transitions consist of a main line (*M*), center dip (CD) and extra line (*X*). Finally, the 25_4-25_5 transition in the bottom trace shows that only the $25_{4,22}$ level is perturbed.

line (X), and a center dip (CD). The other asymmetry component is unperturbed and gives rise to a single line in the bottom trace.

The transitions to levels involving $K'_a = 1-4$ generally consist of two resolved lines, split by the effect of asymmetry. Calculations show that transitions to most levels above $K'_a = 4$ should not show any asymmetry splittings, so that in the absence of perturbations, these transitions are single lines, even at sub-Doppler resolution. In many cases, small splittings of these levels are observed, indicating small upper state perturbations where the extra lines are too weak to detect.

B. Collisional effects

Variations in pressure were found to affect some features in the spectra and not others. In the case of genuine center dips arising from transitions which have a ground state level in common, decreasing the pressure did not appreciably change the relative intensities of the main, extra, or center dip lines. However, there were many spectra containing center dips between transitions which do not have a level in common. For example, closely spaced asymmetry doublets which are unresolved in Doppler-limited spectra often exhibited center dips between the two asymmetry components, in the absence of a common level. A clear example is shown in Fig. 2, which also shows that the center dip is pressure dependent and would not be detectable at very low pressures. This is a collision-induced center dip, caused by collisional population transfer between neighboring levels.^{23–25}

Further complications arise in the case where there are asymmetry splittings and extra lines. Figure 3 shows an example of a situation where the pair of transitions $16_{6,10}-16_{5,11}$ and $16_{6,11}-16_{5,12}$ should not be resolved in the sub-Doppler spectrum, since the asymmetry splittings in the



FIG. 2. The effect of pressure on the 2_2-1_1 transition. The two strong transitions do not have an upper or lower state in common and so the center dip must be due to a collision-induced transfer of energy between the nearly degenerate upper state energy levels. The strongly pressure dependent center dip intensity verifies this interpretation.

upper and lower states are both less than 1 MHz. However, one of the upper state components is shifted to lower energy by a perturbing level, giving rise to an extra line and a strong center dip. There are also weaker collisional center dips between each of the two main lines and between the extra line and the unperturbed transition. The stronger "genuine" center dips have intensities close to the geometric mean of the two related transitions, while the collisional center dips are much weaker in the pressure regime of the present experiments. Unfortunately, in the case shown in Fig. 3, it is not possible to determine from the data which upper state asymmetry component is perturbed. In some cases, this can be



FIG. 3. The sub-Doppler spectrum of the $16_{6}-15_{5}$ transition. The transitions from the ground state to the S_{1} state energy levels are the main lines M_{a} and M_{b} . The subscripts are used to denote the different parities of the lower states involved in each transition. The M_{a} transition (indicated by a thicker leader) has a genuine center dip (dashed line) and an extra line (X_{a}) associated with it. The center dip intensity is the geometric mean of the line and extra line, so it is quite strong. The leaders below the spectrum identify collision-induced center dips between levels of different lower state parity.



FIG. 4. The sub-Doppler spectrum of the 6_4-5_3 [$r_{3}(5)$] transition showing very complex structure, with 16 assigned features. The "a" parity lines consist of the main line (10), two extra lines (3 and 16), and associated center dips. The "b" parity lines consist of the main line (14), two extra lines (1 and 6), and associated center dips. The lines labeled "a to b center dips" are collision-induced center dips connecting upper state levels as shown by the diagonal lines. The assignments are given in more detail in Table I.

done by ground state combination differences or measured line frequencies, if the asymmetry splitting is appreciable in either the lower or upper state.

The $rR_3(5)$ transition, which we reported previously,¹⁹ but did not analyze in detail, is shown in Fig. 4. Figure 4 serves to illustrate the analysis of a complex spectrum with asymmetry splittings, more than one extra line, and many center dips. The various features are labeled 1-16 for clarity. In the absence of any perturbations, calculations show that this spectrum should be a single line made up of the unresolved $6_{4,2}-5_{3,3}$ and $6_{4,3}-5_{3,2}$ transitions. On the basis of intensity and the pattern of extra lines, peaks 10 and 14 are the main lines of parity "a" and "b," respectively. These lines are due to transitions from S_0 to perturbed S_1 rotational levels. Peak 10 has extra lines 3 and 16 associated with it, and these are accompanied by strong genuine center dips (lines 7 and 13). Similarly, peak 14 has extra lines 6 and 1 to lower energy and center dips 9 and 11. Finally, lines 1 and 6 are connected by a center dip because they are extra lines which both have the same lower level.

The remainder of the lines can be satisfactorily explained as collision-induced center dips. They are relatively weak compared to the transitions that they connect and involve levels which have opposite parities. The complete set of assignments is summarized in Table I. Despite the rather comprehensive picture of the perturbations involved, it is not possible to determine the parities of the main lines in the absence of further information.

C. Determination of the ground state molecular constants

In the process of assigning the observed transitions, it soon became apparent that the best available H_2CS ground state constants² were not sufficient to reproduce many of the ground state combination differences obtainable from the

TABLE I. Wave numbers (in cm^{-1}) and assignments of the lines identified in Fig. 4.

Line	cm ⁻¹	Assignment	Comments				
1	16 824.622 0	$\overline{X_{1b}}$	Extra line associated with M_b				
2	16 824.623 6	cd	Collisional between X_{1b} and X_{2a}				
3	16 824.624 9	X_{2a}	Extra line associated with M_a				
4	16 824.626 6	cd	$X_{1b} - X_{3b}$ center dip				
5	16 824.628 0	cd	Collisional between X_{2a} and X_{3b}				
6	16 824.631 2	X3b	Extra line associated with M_b				
7	16 824.632 0	cd	$X_{2a} - M_a$ center dip				
8	16 824.635 1	cd	Collisional between X_{3b} and M_a				
9	16 824.637 2	cd	$X_{1b} - M_b$ center dip				
10	16 824.639 0	Ma	Main line, parity "a"				
11	16 824.641 8	cd	$X_{3b} - M_b$ center dip				
12	16 824.645 7	cd	Collisional between M_a and M_b				
13	16 824.649 3	cd	$M_a - X_{4a}$ center dip				
14 .	16 824.652 4	M_{b}	Main line, parity "b"				
15	16 824.656 1	cd	Collisional between M_b and X_{4a}				
16	16 824.659 7	X _{4a}	Extra line associated with M_a				

sub-Doppler spectra. In particular, $\Delta K'_a = 2$ combination differences showed K_a -dependent discrepancies with maximum values of 3000 MHz at $K''_a = 11$. The difficulty with the ground state constants is that the reported microwave data²⁶ consist only of $\Delta K_a = 0$ transitions with $J \leq 27$ and $K_a \leq 4$. Our combination differences represent a much larger range of K_a and J values and often involve energy differences between K stacks more suited to determining the A, Δ_K , and H_K constants. The $\Delta K''_a = 2$ intervals are conservatively estimated to have a precision of 10 MHz, over a wave number range of 200–400 cm⁻¹, corresponding to a measurement of one part in $0.6-1.2 \times 10^6$, comparable to the original microwave data²⁶ with a precision of one part in $0.4-2 \times 10^6$.

We have refined the ground state constants by a simultaneous, weighted least-squares fit on a data set involving 56 microwave transitions,²⁶ 584 infrared combination differences from the Fourier transform infrared (FTIR) measurements of Johns and Olson,²⁷ and 355 sub-Doppler combination differences. The asymmetric top Hamiltonian used was Watson's A reduction in the I^r representation.²⁸ The microwave and sub-Doppler data were sufficient to determine all of the quartic distortion constants plus H_{κ} , and addition of the IR data only improved the standard deviations of the constants. The sub-Doppler data fit very well, as shown in Fig. 5, with an overall standard deviation of 9 MHz. The resulting ground state constants are given in Table II. They are similar to previous values derived from microwave and optical combination differences² with the major refinement being the inclusion of H_{κ} in the centrifugal distortion constants. It is gratifying that our sub-Doppler measurements are sufficiently precise to improve on constants previously determined largely by microwave data.

D. Determination of the excited state constants

Once the ground state constants had been determined, we attempted to find a sufficient number of unperturbed transitions to obtain the excited state molecular constants. This proved to be quite difficult, since many of the transitions which do not have extra lines within their Doppler width are



FIG. 5. Observed-calculated values for ground state combination differences derived from the sub-Doppler data after least-squares refinement of the ground state constants.

nevertheless perturbed by longer range interactions with triplet state levels. Previously published magnetic rotation spectra² (MRS) proved invaluable for identifying the strongest of these perturbations, although the weaker singlettriplet interactions were not evident in the MRS. Largely by trial and error, a set of 127 upper state energy levels was identified as sufficiently unperturbed to be useful in the fitting procedure. A total of 211 transitions involving these "unperturbed" levels were fit to the asymmetric top Hamiltonian with the ground state constants held fixed, giving an overall standard deviation of 0.000 97 cm⁻¹ (29 MHz). The constants are presented in Table II and a representative set of transitions involving all of the "unperturbed" energy levels is listed in Table III.

A number of tests were done to be sure that the set of unperturbed transitions contained a sufficient range of data to give reliable constants. The upper state constants were used to generate a data set of exact transition frequencies involving the same transitions as those fitted. Small random frequency shifts of the order of the experimental errors were added to the exact frequencies and these synthetic data were fitted again. The results were well within the standard deviations of the original constants. Then these exact and fitted constants were used to predict transition frequencies_other than those in the original data set. The agreement was very satisfactory for transitions with $K'_a \leq 12$.

It is not surprising that the excited state rotational constants obtained in this work are quite close to those reported by Clouthier et al.² from a fit of the Doppler-limited spectrum of the $\tilde{A}^{1}A_{2} - \tilde{X}^{1}A_{1} + 4_{0}^{1}$ absorption band. The small sub-Doppler perturbations would tend to average out over a large number of transitions, so that the mean positions of the upper state energy levels would be very close to their unperturbed values. Indeed, in the original work, aside from the readily recognized local singlet-triplet perturbations, the rest of the rotational lines were found to fit very well, suggesting that there were no further perturbations. It was only when sub-Doppler techniques were first employed⁵ that it was recognized that the spectrum contained many small perturbations due to interactions with the ground state. In this situation, it is difficult to get a reliable set of upper state constants.

E. Spectroscopic perturbations

As discussed in some detail in our previous work,¹⁹ the excited state perturbations have been classified as singletsinglet $(S_1 - S_0)$ or singlet-triplet $(S_1 - T_1)$ depending on the magnitude of the level shift, the occurrence of extra lines within the Doppler width, and particularly the correlation with observed MRS² and Zeeman⁴ activity. The singletsinglet perturbations involve small matrix elements and minute line shifts, and usually show extra lines in the sub-Doppler spectra. The transitions do not have appreciable magnetic effects. The singlet-triplet perturbations have much larger matrix elements $(0.05-0.15 \text{ cm}^{-1})$ and line shifts, and generally show MRS or Zeeman activity. The sub-Doppler structure is usually free of extra lines or, in the case of strong mixing, shows resolved hyperfine structure. In a number of cases, there is evidence for interactions of a single S_1 level with both T_1 and S_0 levels.

One might argue, however implausibly, that the extra lines observed at sub-Doppler resolution are hyperfine splittings due to weak singlet-triplet interactions. This would necessitate a large number of triplet levels with very small

·	Ground	d state	4^1 level of the $\tilde{A}^{-1}A_2$ excited state					
	Ref. 2	This work	Ref. 1	This work				
A .	9.727 1203(11)	9.727 180 ₂ (15)	9.057 15 ^b	9.055 6439(6)				
B	0.590 399 476(5)	0.590 399 1.(3)	0.537 785 ^b	0.537 81840(14)				
С	0.555 442 566(5)	0.555 442 26(3)	0.510 176 ^b	0.510 14342(14)				
$10^4 \Delta_{\kappa}$	7.62257(20)	7.780 768(26)	4.242(39)	3.23272(15)				
$10^5 \Delta_{JK}$	1.742 ₈₀ (6)	1.737 747(17)	2.091(16)	2.116(5)				
$10^7 \Delta_I$	6.4887(6)	6.45763(14)	8.314(23)	8.29666(40)				
$10^{5}\delta_{K}$	1.24049(6)	1.240794(18)	1.3 ^b	$1.7_{31}(4)$				
$10^8 \delta_I$	$4.020_{43}(5)$	$4.018_{08}(3)$	4.4 ^b	6.623(6)				
$10^{7}H_{K}$	0.0 ^b	1.82963(15)	0.0 ^b	$-4.80_{83}(10)$				
<i>T</i> ₀		1.1.1	16 765.735 3(6)	16 765.735 7(6)				

^aThe error limits are 3σ and are right justified to the last digit on the line; sufficient additional digits are quoted to reproduce the data with full accuracy. ^bConstant fixed in fitting.

TABLE II.	Rotational constants for H_2CS (in cm ⁻¹). ^a	
		_
	Ground state	

TABLE III. Wave numbers (in cm⁻¹), assignments, and residuals of transitions involving unperturbed levels in the upper state of the 4_0^1 band of H₂CS.

TABLE III. (Continued.)

		, unpert			ine upp	er state of the 4_0 t	band of H_2CS .		<i>K'</i> .	K'.	J″	<i>K</i> "	 K"	Obs.	ObsCalc.
J'	K'_a	K_c'	J″	K''_a	K_c''	Obs.	ObsCalc.	10	a	15		a	19	16 779 102 2	0.0006
		0		1	1	16 755 452 7	-0.0012	19	4	16	20	2	10	10 / /0.192 3	-0.0003
1	ñ	1	1	1	ò	16 756 465 9	-0.0012	22	4	18	23	3	21	16 768 521 2	0.0002
2	õ	2	3	1	3	16 752.955 5	-0.0006	22	4	19	21	3	18	16 820.028 7	0.0010
3	ŏ	3	4	1	4	16 751.586 6	0.0001	24	4	20	23	3	21	16 817.679 4	0.0015
4	õ	4	4	1	3	16 755.427 8	-0.0007	24	4	21	23	3	20	16 817.637 5	0.0002
6	Õ	6	7	ĩ	7	16 746.994 2	0.0001	26	4	22	26	3	23	16 785.051 8	0.0014
8	0	8	9	1	9	16 743.527 7	0.0006	27	4	23	28	3	26	16 750.397 1	0.0003
26	0	26	25	1	25	16 756.636 7	-0.0002	28	4	25	28	3	26	16 779.665 6	0.0014
27	0	27	26	1	26	16 755.434 0	-0.0005	29	4	25	30	5	26	16 596.861 7	0.0006
3	1	2	4	2	3	16 732.575 6	-0.0003	30	4	26	30	3	27	16 773.606 0	0.0030
3	1	3	2	0	2	16 777.035 0	0.0008	5	5	0	6	6	1	16 641.932 0	0.0002
4	1	3	5	2	4	16 731.095 3	0.0008	8	5	3	7	4	4	16 838.164 1	-0.0018
4	1	4	5	2	3	16 730.817 1	0.0021	10	5	5	10	4	6	16 827.131 3	-0.0012
5	1	5	4	0	4	16 778.322 1	0.0011	11	-5	6	10	4	7	16 838.643 9	-0.0009
б	1	5	6	2	4	16 735.891 8	0.0006	14	5	9	14	6	8	16 639.997 5	-0.0012
7	1	6	7	2	5	16 735.296 7	-0.0007	21	5	16	20	4	17	16 833.783 6	-0.0015
17	1	17	16	0	16	16 776.868 8	-0.0007	7	6	1	8	7	2	16 613.833 9	-0.0001
18	1	18	19	0	19	16 733.905 0	0.0002	9	6	3	9	5	4	16 839.624 2	-0.0004
20	1	20	19	0	19	16 774.151 9	0.0001	11	6	5	11	5	6	16 837.553 5	0.0009
21	1	21	20	0	20	16 773.049 2	0.0012	13	6	7	12	5	8	16 849.965 0	-0.0005
28	1	28	27	0	27	16 762.674 3	-0.0011	14	6	8	13	5	9	16 849.727 4	0.0006
29	1	29	28	0	28	16 /60.82/ 2	-0.0017	15	6	9	14	5	10	16 849.389 1	0.0003
21	1	29	31	2	30	16 725 207 0	-0.0011	10	0 4	11	10	5	12	16 848,415 0	0.0009
51	1	30	51	1	51	16 700 202 2	-0.0010	10	0	12	17	5	13	10 847.7779	0.0007
6	2	4 5`	6	1 1	5	16 780 012 2	0.001	20	6	13	10	5	14	16 846 204 2	0.0001
22	2	20	22	1	21	16 762 300 6	0.0008	20	6	14	20	5	15	16 845 265 5	-0.0007
23	2	21	22	· 7	20	16 691 003 9	-0.0000	21.	6	15	20	5	10	16 844 229 3	0.0011
23	2	22	23	1	23	16 768 560 3	0.0001	24	6	18	24	7	17	16 596 342 8	0.0000
24	2	22	24	3	21	16 688 732 7	-0.0009	27	6	21	26	5	22	16 837 531 9	-0.0008
24	2	23	24	3	22	16 687.820 2	-0.0011	28	6	22	20	5	23	16 835.889 4	-0.0006
25	2	23	25	1	24	16 754.524 1	0.0019	29	6	23	29	5	24	16 800.987 1	0.0007
25	2	24	25	1	25	16 764.640 6	-0.0007	30	6	24	29	5	25	16 832.299 2	-0.0007
26	2	25	26	3	24	16 682.699 3	0.0002	9	8	2	10	9	1	16 557.996 6	0.0011
28	2	26	28	3	25	16 678.754 5	-0.0005	11	8	3	10	7	4	16 869.651 9	0.0000
28	2	27	28	3	26	16 677.155 0	0.0006	15.	8	7	14	7	8	16 868,874 4	-0.0003
14	3	11	14	4	10	16 685.960 5	-0.0003	16	8	8	15	7	9	16 868.431 5	0.0003
14	3	12	14	4	11	16 685.959 5	-0.0001	19	8	11	18	7	12	16 866.500 0	-0.0014
17	3	15	16	2	14	16 810.102 2	0.0001	20	8	12	19	7	13	16 865.655 7	-0.0023
22	3	19	22	4	18	16 671.482 5	-0.0017	25	8	18	. 26	9	-17	16 512 289 3	0.0004
22	3	20	22	4	19	16 6/1.465 7	-0.0015	30	8	22	29	7	23	16 851.684 4	0.0002
23	3	20	23	4	19	16 669.234 9	0.0009	34	8	26	34	10	27	16 804.438 3	-0.0001
20 24	2	21	25	4	20	16 748 207 1	-0.0019	10	9	U 1	10	10	1	16 530.770 7	-0.0000
24 94	3	22	23	2.	24	16 202 046 0	-0.0008	10	9	2	10	10	2	16 977 724 0	0.0002
25	3	22	25	4	21	16 664 439 5	-0.0001	12	á	3	11	8	- 4	16 877 676 8	0.0004
25	3	23	25	2	24	16 774 334 5	-0.0008	13	. 9	5	14	10	4	16 521 700 8	0.0010
26	3	23	26	2	24	16 769.948 8	0.0009	14	9	5	13	8	6	16 877.281 2	0.0002
26	3	24	25	2	23	16 799.863 9	0.0002	16	9	7	- 17	10	8	16 513.867 4	-0.0003
28	3	25	28	2	26	16 764.087 9	0.0013	10	10	- `1	9	9	0	16 884.664 3	-0.0009
28	3	26	28	2	27	16 766.570 3	0.0015	12	10	2	11	. 9	3	16 884.663 9	0.0009
29	3	. 26	29	2	27	16 760.979 5	~ 0.0020	14	10	4	13	. 9	5	16 884.259 9	-0.0015
30	3	27	30	4	26	16 650.747 3	0.0024	16	10	6,	15	9	7	16 883.459 3	-0.0003
7	4	4	6	3	3	16.825.097 2	-0.0009	17	10	7,	16	9	8	16 882.907 9	-0.0005
10	4	6	10	3	7	16 814.422 0	0.0000	18	10	8	17	9	9	16 882.257 1	0.0002
11	4	7	10	3	8	16 825.939 7	0.0006	19	10	· 9	18	´ 9	10 `	16 881.503 2	-0.0018
11	4	8	10	3	7	16 825.938 9	0.0001	20	10	10	19	9	11	16 880.653 9	0.0013
14	4	10	13	3	11	16 825.530 4	0.0003			·····					
14	4	11	13	3	10	16 825.528 1	-0.0006	. • 1			· ,			; o	
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16	4 4	12	15	2	12	16 824.700 3	-0.000	$S_1 - 7$	T₁ ma	trix ele	ments	in the	vicini	ity of the 4^1 le	vel. How-
17	4	13	16	3	14	16 824 226 8	0.0010	ever	the d	lensity	of triv	olet lev	els in	this region is	much too
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of observed perturbations. Furthermore, the matrix elements

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FIG. 6. Plots of the residuals (observed-calculated) for various asymmetry split levels in the $\tilde{A}^{-1}A_2$ 4¹ state of H₂CS. The open circles denote "unperturbed" levels included in the least-squares determination of the upper state rotational constants. Closed circles denote perturbed levels not included in the fit, and extra levels are designated by "X". The U and L notations refers to the upper and lower asymmetry components, respectively. The J'=6 level has been omitted from the plot for $K'_a=4$, since the parities of the levels could not be assigned.

would have to be at least two orders of magnitude smaller than those responsible for the known singlet-triplet perturbations in the S_1 0⁰ and 4¹ levels. It is unlikely that the rotational or vibrational overlap components of the singlettriplet matrix elements would change so substantially over such a small energy range. In the few cases where hyperfine splittings due to strong interactions with triplet state levels have been observed, both in the present work and in previous studies,^{4,13,19} characteristic three-line patterns of lines are found. In the levels we have assigned as perturbed by ground state levels, we have not observed any such regularities suggestive of hyperfine structure. The absence of Zeeman or MRS effects on these perturbed levels in S_1 is also good evidence that the triplet state is not involved. Finally, as shall be shown, the numbers of perturbations and their J dependence can be very satisfactorily explained by a model which explicitly considers interactions with high vibrational levels of the ground state.

⁻ The complete set of assignments, including the observed extra lines and observed minus calculated values, are summarized in a table which has been deposited with the Physics Auxiliary Publication Service (PAPS) of the American Institute of Physics.²⁹ The level shifts obtained by comparing the observed transition frequencies with those calculated using the constants in Table II are shown in Figs. 6 and 7. A small number of levels in K_a =0, 1, 2, and 3 display large pertur-

FIG. 7. Plots of the residuals (observed-calculated) for various levels calculated to have negligible asymmetry splittings in the $\tilde{A} \, {}^{1}A_{2} \, 4^{1}$ state of H₂CS. In cases where asymmetry splittings are observed due to perturbations, the residuals are averages over the two lines. The symbols are the same as in Fig. 6.

bations involving transitions which show MRS activity and are clearly singlet-triplet in nature. In $K_a=7$, there is a pronounced resonance, with the maximum perturbation occurring at J=10, 11, and 12, which also show MRS activity. The perturbations at high J in $K_a=5$ may also be singlet-triplet in nature, although there is no MRS or Zeeman evidence to confirm this notion. The most common types of perturbations observed are the small level shifts associated with S_1-S_0 interactions. These are liberally sprinkled throughout the 4¹ manifold of levels and show up as extra lines, splittings of transitions to higher K_a levels, or center dips in cases where the extra lines are too weak to observe.

F. Interactions with levels of the triplet state

Most of the stronger perturbations observed in this work that can be ascribed to singlet-triplet interactions have been discussed in detail by Fung *et al.*⁴ They concluded that the MRS and Zeeman-active transitions involved perturbations by the $4^{2}6^{2}$, 6^{3} , and $2^{1}3^{1}$ vibrational levels of the excited triplet state with vibronic origins of 16 736.8±2, 16 775.0 ±2, and 16 686.8±2 cm⁻¹, respectively. We have recalculated the vibronic origins of the perturbing levels based on more recent triplet state vibrational data,¹² as summarized in Table IV, assuming that the rotational structure of each triplet level is identical to that of the vibrationless level.³⁰ We find that the mechanisms of Fung *et al.*⁴ not only explain the magnetically sensitive lines, but also account for some of the

TABLE IV. Vibrational frequencies of thioformaldehyde in various electronic states (in cm^{-1}).

Vibration	$\tilde{X}^{1}A_{1}$	$\tilde{a}^{3}A_{2}$	$\tilde{A}^{-1}A_2$
$\nu_{\rm I}$ (symmetric C–H stretch)	2971.0 ^a	(2962) ^b	3033.4 ^d
ν_2 (CH ₂ bend)	1457.3	1318.6°	1334.5
ν_3 (C=S stretch)	1059.2	861.7	819.7
ν_4 (out-of-plane bend)	990.2	See below	See below
ν_5 (antisymmetric C–H stretch)	3024.6	(3078) ^b	3054.9
v_6 (CH ₂ rock)	991.0	762.3	785.2
4 ¹		326 ^e	370.3 ^f
4 ²		710.5	835.3
4 ³		1124.9	1339.7
4 ⁴		1548.8	1856.1
4 ⁵		1968.9	2371.8

*Ground state frequencies from Ref. 27.

^bAb initio value (Ref. 28).

"Experimental values from Ref. 12.

^dExperimental values from Ref. 11.

Calculated values from Ref. 11.

^fCalculated values from Ref. 12.

other strongly perturbed lines in the sub-Doppler spectra. In particular, the perturbation of J=20 in the upper asymmetry component of $K_a=1$ can be readily found to be due to the $20,20_{2,18}$ (J,N_{K_a,K_c}) rotational level of 4^26^2 with a vibronic origin of 16 737.4 cm⁻¹, in agreement with previous values.⁴ Similarly, the small avoided crossing at J=19 in $K_a=3$ can be explained by the interaction with the F_1 component of 6^3 , although the rotational structure of the triplet level appears perturbed by the 4^46^1 level which is slightly higher in energy.

The strong resonance in $K_a=7$ cannot be explained on the basis of the previous mechanisms. The most strongly perturbed transitions (J'=10, 11, and 12) are magnetically sensitive and it is most likely that a single triplet state perturbing level is involved. On this basis, we calculate that the perturbation is due to the $K_a=6$ (F_1) rotational levels of a triplet state with a_1 vibrational symmetry and a vibronic origin of 16 878 cm⁻¹. The only candidate is the $3^{1}6^{2}$ level with a calculated vibronic origin of 16 894 cm⁻¹, based on $\nu_3=861.7$ cm⁻¹ and $\nu_6=762.3$ cm⁻¹ and the harmonic approximation.¹² Calculations show that the triplet state levels cross $K_a=7$ at a shallow angle, so that a resonance extending over several J values is observed.

There is no direct spin-orbit coupling between singlet and triplet states of the same electronic symmetry, but Stevens and Brand³¹ have discussed two second-order mechanisms by which perturbations can occur. States of the same orbital and vibronic symmetry can couple via a spinorbit orbital-rotation mechanism. For states in which the product of the vibronic symmetry species contains the species of a rotation, a vibronic spin-orbit mechanism is appropriate. The extensive singlet-triplet perturbations in the 0_0^0 band of H₂CS have been shown to involve a vibronic spinorbit mechanism³ with rotational level dependent matrix elements of 0.25-0.45 cm⁻¹. In the 4_0^1 band, all of the perturbations involve triplet vibrational levels with symmetry species different than the S_1 4¹ level, so the mechanism is also of the vibronic spin-orbit type. The matrix elements are of the order of 0.05-0.15 cm⁻¹, based on the magnitudes of



FIG. 8. Histograms of the percentage of S_1 levels of a given J which show evidence of sub-Doppler perturbations involving the ground state. In (a) the experimentally observed values are shown; for J=0, 1, and 2, the percentage is zero. In (b), the percentages for a single calculation are presented. The cross-hatched areas are with rotation-vibration mixing in the ground state; the black areas are calculated in the absence of such mixing. In (c), the percentages are shown for the average of 100 calculations in which small random energy shifts were added to each level to simulate Coriolis perturbations.

the observed level shifts. The smaller matrix elements in the 4^1 state probably reflect smaller Franck-Condon factors as the energy gap between the S_1 and T_1 states increases.

G. Interactions with levels of the ground state

The small localized perturbations which are not magnetically sensitive are due to interactions with high vibrationrotation levels of the ground state.^{5,19} It is difficult to identify the $S_1 - S_0$ perturbations based solely on the level shifts in the presence of the much stronger singlet-triplet perturbations. An alternative, although less sensitive, measure of interactions with the ground state is simply to count the levels whose transitions show extra lines, center dips, or unexpected splittings within their Doppler width. Of the 350 distinct levels observed up to $K'_a = 30$, about 185, or 53%, are of this type. This is a lower limit to the percentage of levels which are perturbed, since small or long range interactions will not give observable center dips or extra lines. Despite our conservative estimate, a remarkably high percentage of the observed excited state levels is found to be mixed with levels of the ground state. Although we have not found any systematic pattern in the magnitude of the perturbations, the percentage of excited state levels which are perturbed shows a distinct variation with J as shown in Fig. 8(a). For J=0, 1, 1

and 2 (a total of nine levels), there are no ground state perturbations at all. The percentage rises with J and levels off at about 60% (plus noise) at higher J values.

By using a simple model, it is possible to reproduce both the distribution and magnitudes of the percentages shown in Fig. 8(a). It involves an approximate calculation of the number of ground state rovibronic levels of the correct symmetry and quantum numbers within the proximity of each excited state level. We begin with some theoretical considerations.

The interaction of the excited S_1 state with high rovibronic levels of the ground state occurs through the breakdown of the Born-Oppenheimer approximation and involves the nuclear kinetic energy operator. Direct vibronic coupling between the $\tilde{X}^{-1}A_1$ and $\tilde{A}^{-1}A_2$ states cannot occur, since they differ by more than the species of one of the normal vibrations. It is then necessary to consider higher order interactions involving other electronic states. The 4_0^1 band in the $\tilde{A} - \tilde{X}$ system of H₂CS gains intensity by vibronic interaction with a higher ${}^{1}B_{2}$ state. The vibronic coupling of this ${}^{1}B_{2}$ state with the ground state leads to a second-order mixing of the A and X states, such that only B_2 vibrational levels of the ground state are involved. Assuming that the ground state levels are not strongly mixed by Coriolis interactions, the rotational selection rule for the $S_1 - S_0$ interaction is $\Delta J = 0$ and $\Delta K_a = 0.32$ However, it is likely that substantial rotationinduced vibrational mixing does occur in the ground state. These interactions tend to destroy the goodness of the K_a , K_c , and zero-order vibrational quantum numbers, preserving only the total vibration-rotation symmetry.³³ The general selection rules would then be $\Delta J=0$ and only levels of the same overall rovibronic symmetry species can interact.³⁴

In our computer model, we first generated all the ground state vibrational levels of H_2CS up to 18 100 cm⁻¹, the maximum energy observed in the S_1 state. The vibrational frequencies given in Table IV were used in the harmonic approximation, since there is little information on the vibrational anharmonicities of thioformaldehyde. We obtained a level density (ρ_v) of three to four levels per cm⁻¹ in the 17 000 to 18 100 cm^{-1} range, with the levels distributed almost equally among the four possible symmetry species, in agreement with estimates based on less direct methods.35,36 To each vibrational level was appended a set of rotational levels, up to J=30 and $K_{a}=30$, calculated using the ground state rotational constants (Table II). In the process, the rotational quantum numbers $(J, K_a, and K_c)$ and overall rotation-vibration symmetry of each level were recorded for future use. The degeneracies associated with nuclear spin functions and the 2J+1 components of the total angular momentum along the space-fixed Z axis were not included, since they only affect the rate of internal conversion, not the number of perturbations.

Finally, the energy, J value, and symmetry of each excited state rotational level were compared with those in the manifold of ground state levels to determine if there were any appropriate ground state levels close enough to perturb the excited state level. The energy range over which the perturbations would be detectable was determined by the following arguments. The sub-Doppler spectra were scanned over the Doppler width of each rotational line (~0.07 cm⁻¹)

to baseline), so that only those extra lines or center dips appearing within about ± 0.035 cm⁻¹ of the line center would signal a perturbation. Beyond $K_a = 4$, detectable splittings in the asymmetry doublets were taken as evidence for a perturbation in at least one of the quasidegenerate levels. In previous work,¹⁹ we found $S_1 - S_0$ matrix elements in the range of 0.001-0.01 cm⁻¹ and the maximum level shifts observed in this work are about 0.01 cm^{-1} . For levels with an unperturbed separation of 0.035 cm⁻¹ and matrix elements of $0.01-0.001 \text{ cm}^{-1}$, perturbation theory gives level shifts of 0.0030-0.00003 cm⁻¹. The former would be readily detectable in the sub-Doppler spectra, while the latter are too small to be observed. From these considerations, we conclude that S_0 levels within about ± 0.035 cm⁻¹ of an S_1 level would be effective in generating detectable perturbations.

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Using the above criteria, we first generated a theoretical plot of the percentage of S_1 levels which would be perturbed by at least one S_0 level within the limitation of negligible rotation-vibration mixing in the ground state. The result, shown in Fig. 8(b), is that very few perturbations are expected. Clearly, this constraint is unrealistic. We then eliminated the $\Delta K_a=0$ selection rule (assuming strong rotation-vibration mixing in the ground state) and redid the calculation with the result also shown in Fig. 8(b). The model predicts very few perturbations at low J, increasing with J and averaging about 60% at high J, as is observed experimentally.

Several tests were done to check the effect of the various assumptions built into the model. The effective energy gap between S_1 and S_0 levels was increased 100% to reflect longer range interactions. As expected, the number of perturbations increased, but the relative trends were the same. The effect of changes in the rotational constants with vibrational energy and the scrambling effects of rotation-vibration mixing were simulated by adding a random shift in the range of $0-1 \text{ cm}^{-1}$ to each ground state level before calculating the perturbation diagrams, with no significant change in the results. In order to remove the "noise" evident in both the experimental and theoretical plots, averages of 100 individual calculations with random energy shifts were done, yielding the smooth histograms shown in Fig. 8(c). These show that, on average, the $\Delta K_a = 0$ selection rule is too restrictive and that rotation-vibration mixing in the ground state leads to a steadily increasing percentage of perturbed levels which levels out at high J values.

Despite the simplistic nature of the model, the qualitative, and to some extent quantitative, aspects of the experimental results are reproduced. This success is most likely due to two factors. First, the experimental percentages are over several K_a levels for each J, which tends to smooth out fluctuations. The model can predict what percentage of a group of levels will be perturbed, but is of little use in predicting whether a particular S_1 rotational level will be perturbed. Second, the calculated results involve such large numbers of ground state levels that unrealistic simplifications tend to be lost in the averaging that occurs.

The model calculations give strong evidence that there is substantial rotation-vibration mixing in the ground state of

 H_2CS at 17 000 cm⁻¹. This is not unexpected since there is other experimental evidence that K_a is not a good quantum number in the high vibrational levels of the ground state. Ramsay and co-workers37 have argued that the number of microwave-optical double resonance (MODR) transitions observed in the $S_1 4^1$ level of H₂CS is larger than expected, unless K_a is not a good quantum number. They have reached the same conclusion based on studies of the Zeeman effect on the MODR signals.⁹ Since Coriolis coupling within the ground state manifold conserves only J, the effective density of states of the correct rotation-vibration symmetry would be $(2J+1)\rho_{\nu}/4$.¹³ With $\rho_{\nu}=3-4$ per cm⁻¹, this gives a J-dependent density of 0.05-0.07 levels at J=0, escalating to 3.2-4.3 at J=30 over a 0.07 cm⁻¹ interval. The density of states argument predicts a small chance of a perturbation at low J, but a strong likelihood of perturbations at high J, in general accord with experiment.

The distribution of perturbing ground state levels must be uneven or "lumpy," since there are many examples of high J values in S_1 that are not measurably perturbed. This is consistent with the level structure envisioned by Dunlop and Clouthier¹³ to rationalize their measurements of collisionfree single rotational level lifetimes and relative quantum yields of fluorescence of the 4¹ S_1 state. They proposed that the zero-order ground state levels are connected by Coriolis and Fermi interactions to form an uneven background. The mixing of S_1 and S_0 levels then relies on accidental coincidences between levels. What was not envisioned at that time was the great extent of the perturbations.

IV. DISCUSSION

In this paper, we report the analysis of the 4_0^1 band of the $\tilde{A} {}^1A_2 - \tilde{X} {}^1A_1$ system of H₂CS studied at sub-Doppler resolution. There are three interesting conclusions. The first is that all the singlet-triplet perturbations in the upper state can be ascribed to a vibronic spin-orbit mechanism with matrix elements of 0.05-0.15 cm⁻¹. The second is that a **majority** of the upper state levels, over a large range of J and K_a, are perturbed by the ground state. The final conclusion is that the density of ground state perturbations can only be rationalized if there is rotation-induced vibrational mixing in the high vibrational levels of the ground state.

The finding that the singlet-triplet perturbations are due to a vibronic spin-orbit mechanism is not surprising. The extensive perturbations in the 0_0^0 band have been thoroughly explained using the same mechanism.³ In fact, this type of interaction has been found in all the carbonyl compounds whose singlet-triplet perturbations have been thoroughly characterized. In propynal, Zeeman³⁸ and quantum beat studies³⁹ have shown that small singlet-triplet perturbations arise from vibronic spin-orbit coupling with matrix elements⁴⁰ on the order of a few megahertz. Matrix elements of the same order of magnitude were obtained from the quantum beat spectra of biacetyl⁴¹ and methylglyoxal,⁴² although no one mechanism appeared to dominate the interaction.⁴³ In glyoxal, level anticrossing spectroscopy^{44,45} has been used to show that the vibronic spin-orbit mechanism is the dominant contribution to the singlet-triplet interaction, with matrix elements of 1-300 MHz. Finally, in formaldehyde, singlet-triplet perturbations have been studied for a variety of vibrational levels.⁴⁶ Generally, only a few rotational levels per S_1 vibrational level are coupled to adjacent triplet levels, with matrix elements of 0.01-0.10 cm⁻¹. On the basis of the vibronic symmetries of the perturbing states, vibronic spin-orbit coupling appears to predominate. The only exception appears to be the more extensive perturbations in the $2_0^2 4_0^1$ band, for which a complex mechanism involving vibronic spin-orbit and spin-orbit orbital-rotation interactions has been proposed.⁴⁷ However, this mechanism has been questioned by further absorption and magnetic rotation studies.⁴⁸

The data suggest that vibronic spin-orbit coupling is the dominant mechanism for the interaction of the singlet and triplet n, π^* states of the carbonyl and thiocarbonyl compounds. Stevens and Brand³¹ suggest that the vibronic spin-orbit matrix elements should be larger than the spin-rotation elements, and this is borne out by quantum chemical order of magnitude calculations for propynal.³⁹ The large differences in the singlet-triplet coupling matrix elements in the various molecules are striking. Thioformaldehyde and propynal have very similar singlet-triplet energy gaps (1888 vs 2035 cm⁻¹), but the matrix elements differ by at least two orders of magnitude. Theoretical studies of the electronic and Franck-Condon factors associated with intersystem crossing in these molecules would be very helpful in understanding these marked variations.

The most interesting aspects of the present work relate to the coupling of the excited state to high vibrational levels of the ground state. The extent of such interactions is astonishing. At least 53% of the S_1 levels surveyed show definite evidence of ground state effects. If one considers longer range interactions not probed by the sub-Doppler experiments, it is not inconceivable that most, if not all, of the excited state rotational levels are perturbed in some fashion. Since the density of S_0 vibrational levels in the vicinity of S_1 is still quite low, the large numbers of perturbations imply that there is rotation-induced vibrational mixing in the ground state, as discussed earlier. Elegant stimulated emission pumping (SEP) experiments on formaldehyde³³ have shown that the vibrational and K_a quantum numbers are compromised at ground state energies as low as 7400 cm^{-1} . Infrared fluorescence measurements involving the C-H stretching modes of a variety of molecules have shown a threshold for vibrational state mixing of five to 30 rovibronic states per cm⁻¹ in the 1000-6000 cm⁻¹ energy range.⁴⁹ Clearly, thioformaldehyde at $17\,000 \text{ cm}^{-1}$ is above this threshold.

At sub-Doppler resolution, the S_1 state of thioformaldehyde is a classic example of the disintegration of a regular spectrum due to the interaction with a dense manifold of perturbing levels. Similar effects are observed in the sub-Doppler spectrum of the BO₂ molecule⁵⁰ at comparable excited state energies. In both cases, we are seeing the genesis of chaotic behavior, where large numbers of interstate couplings occur at relatively low energies. It is likely that this phenomenon is widespread in polyatomic molecules, although detecting it is still quite difficult. The implications for high resolution spectroscopy and excited state dynamics are substantial.

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