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Observations of ortho- and para-thioformaldehyde

F. F. Gardner[1, 2], B. Höglund[3], C. Shukre[2, 4], A. A. Stark[5], and T. L. Wilson[1]

[1] Max-Planck-Institut für Radioastronomie, Auf dem Hügel 69, D-5300 Bonn 1, Federal Republic of Germany
[2] Division of Radiophysics, CSIRO, P.O. Box 76, Epping, N.S.W. 2121, Australia
[3] Onsala Space Observatory, Onsala S-430 34, Sweden
[4] Raman Research Institute, Bangalore 560080, India
[5] AT&T Bell Laboratories, Holmdel, NJ 07733, USA

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Summary. Observations of the $3_{12}-2_{11}$ and $3_{13}-2_{12}$ transitions of ortho and the $3_{03}-2_{02}$ transitions of para H_2CS were made with the Onsala and AT&T Bell Laboratories telescopes. The most precise results, for a beamwidth of 1'.8, were the para (103 GHz) to ortho (104 GHz) line ratios of 0.51 ± 0.04 for Orion and 0.44 ± 0.05 for DR21 (OH). A higher but less accurate ratio of 0.57 ± 0.08 was obtained for DR21 (OH) observed with the smaller 0'.6 beam. The ortho/para ratios are quite close to the values of ~ 0.56 derived from an LVG analysis, with the usual densities, kinetic temperatures and collision rates appropriate to H_2CO cloud molecules, assuming a true para/ortho abundance ratio of 1 : 3. Observations of the ^{34}S isotope of H_2CS towards Orion gave a line ratio $H_2C^{32}S/H_2C^{34}S$ of 15^{+5}_{-3} for the $3_{12}-2_{12}$ transition, not significantly different from the terrestrial $[^{32}S]/[^{34}S]$ value of 22. Revised estimates of the rest frequencies of the various thioformaldehyde lines observed are given.

Key words: interstellar medium: abundances – molecules

1. Introduction

The nuclear spins of the symmetrically placed hydrogen atoms cause a division of the rotational energy levels of molecules such as H_2CS and H_2CO into para (spins anti-parallel) and ortho forms, which can be considered as two distinct species. The two cannot be interconverted by radiative transitions or by non-reactive collisions, and according to Kahane et al. (1984) the ratio of their abundances is determined by the temperatures at which the formation steps take place. They have considered the case of H_2CO. Similar processes would be involved in H_2CS, although the reactions and time scales in its formation are different (see Prasad and Huntress, 1982).

It was considered that observations of H_2CS transitions would contribute to our understanding of the general ortho/para relationship. The interpretation would not be complicated by the existence of high interstellar optical depths, as is the case with H_2CO; in addition the $J = 3-2$ lines of H_2CS occur at ~ 100 GHz, where water vapor absorption in the atmosphere is fairly low, and so are favorable for observation. Published data for H_2CS towards a number of sources are available only for the $3_{12}-2_{11}$ line at 104 GHz (Liszt, 1978) and the $2_{11}-2_{12}$ K-doublet line at 3 GHz (Gardner et al., 1980). The arrangement of energy levels for H_2CS is very similar to that for H_2CO except that the separations are smaller. See, e.g., Henkel et al. (1980) for a diagram of energy levels in H_2CO.

2. Observations

The transitions concerned and the frequencies, from Johnson et al. (1972), are given in Table 1. The initial observations were made with the 20-m telescope of the Onsala Space Observatory in February 1982. At 100 GHz the beamwidth was 36″ and the system temperature of the SSB receiving system about 250 K. The main beam efficiency including radome but not atmospheric losses was estimated as 27% from scans through Jupiter with the usually assumed disk temperature of 170 K. Telescope position switching was used for most of the observations. Spectra were obtained with a bank of 256 × 250 kHz filters. Absolute pointing errors should not exceed 20″. Tracking and day-to-day variability are $\sim 5''$.

The two ortho lines were observed towards seven sources. There was no systematic difference between the intensities at the two frequencies 3 GHz apart and averages for the two transitions are given in Table 2. Intensities are in units of "corrected" antenna temperature, T_A^*, corresponding to a scale of main beam brightness temperature in the Rayleigh-Jeans limit. Limited mapping was carried out for three of the sources. Estimates of peak position and intensity are given in Table 2. Liszt (1978) has made observations of the $3_{12}-2_{11}$ line of H_2CS with the 1'.1 beam of the 11-m NRAO telescope. His values are included in column 10 of the Table for sources in common [the intensities are given in units of radiation intensity $I(K)$; this corresponds to the definition of T_a^* we adopted]. The two sets of intensities are reasonably consistent when account is taken of the different beamwidths.

It was intended to take measurements of the para H_2CS line towards the four strongest sources, W3 (OH), Orion-KL, W51, and DR21 (OH). Unfortunately, after observations of the first source, DR21 (OH), the phase-locking of the local oscillator became erratic and subsequently failed completely. Thus we obtained a reasonable result for DR21 (OH) and a lower limit for Orion-KL. The local oscillator frequency required for the 103 GHz line occurred in the overlap between the ranges of the two klystrons available at Onsala, and as no alternative L.O. source was available the program could not be completed. However, observations of DR21 (OH) and Orion were made subsequently with the AT & T Bell Labs 7-m telescope and a larger beam. The antenna has a primary beam efficiency of 0.89 and a beamsize of 105″ at 104 GHz. The receiver was an SIS mixer in WR-8 waveguide followed by a 1.2 to 1.7 GHz IF amplifier, operated at 4.2 K in a LHe cryostat. The receiver had a DSB noise temperature

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Send offprint requests to: T. L. Wilson

Table 1. H_2CS transitions observed

Transition	Line	Line strength	Frequency Observed[a] (MHz)	Calculated[a] (MHz)	Best estimate[b]
Ortho	$3_{12}-2_{11}$	2.667	104617.04(0.07)	104616.98(0.05)	104616.97(0.04)
	$3_{13}-2_{12}$	2.667	101477.62(0.12)	101477.75(0.05)	101477.75(0.04)
Para	$3_{03}-2_{02}$	3.000	103040.22(0.15)	103040.40(0.05)	103040.36(0.04)
	$3_{21}-2_{20}$	1.667	103051.81(0.28)	103051.79(0.05)	
	$3_{22}-2_{21}$	1.667		103039.85(0.05)	
Ortho $H_2C^{34}S$	$3_{13}-2_{12}$		99774.15(0.05)[c]	99774.052(0.054)[c]	99773.40(0.50)

[a] Johnson et al. (1972)
[b] This paper
[c] Lovas (private communication)

Table 2. Onsala observation of $3_{12}-2_{11}$ (104 GHz) and $3_{13}-2_{12}$ (101 GHz) transitions of H_2CS

Source	Position (1950) (0,0) R.A. (h m s)	Dec. (° ′ ″)	Location of peak intensity	Angular size R.A. (″)	Dec. (″)	Radial velocity (km s^{-1})	Line width (FWHP) (km s^{-1})	Intensity Onsala[a] T_a^*(0,0) (K)	Peak T_a^* (K)	Bell Labs. T_a^* at 104 GHz (K)	Kitt Peak[b] I at 104 GHz (K)
W3 Cont.	02 21 56.7	61 52 30						≦0.1			<0.1
W3 (OH)	02 23 16.8	61 38 52				−46.8	3.2	0.96			
Orion	05 32 47.0	−05 24 20	20″S.	20	50	8.2	3.8	2.55	3.0	0.63	1.42
W49	19 07 52.0	09 01 15				9.1	–	0.13			
W51	19 21 24.0	14 24 52	>20″E., 10″S.			58.9	9.5	0.60	1.3		0.58
DR21	20 37 14.2	42 09 00				− 2.2	–	(0.07)			
DR21 (OH)	20 37 14.0	42 12 00	10″W., 20″S.	<25	>35	− 3.4	4.4	1.15	1.5	0.57	0.78

[a] The peak T_a is estimated
[b] Liszt (1978), using 11-m Kitt Peak telescope of the NRAO

Table 3. Para/ortho line intensity ratio

Source	Para/ortho line ratio 7-m Bell Labs. Observ.	Corrected	20-m Onsala Observ.	Corrected
Orion	0.59±0.04	0.51±0.04	≧0.36	≧0.33
DR21 (OH)	0.50±0.05	0.44±0.05	0.65±0.08	0.56±0.08

of 43 K, and was preceed by a fabry-perot image sideband rejecting filter for a measured SSB noise temperature at the Cassegrain focus of 117 K. The spectrometer was comprised of two sets of filters, 128 × 100 kHz and 128 × 250 kHz. The $3_{12}-2_{11}$ (104 GHz) and the $3_{03}-2_{02}$ (103 GHz) lines were observed with the telescope directed at the positions given in Table 2. Position-switching was employed. The filter channel width used to measure spectra was 100 kHz.

The profiles obtained with the Bell Labs antenna are shown in Fig. 1 and the peak intensities included in Table 2. The velocity fit was found to be optimum when a relative shift of the two rest frequencies of 0.22 MHz (0.64 km s^{-1}) was included. (This agrees within error estimates with the value of 0.21 MHz found at Onsala.) With this shift the fitting of the profiles gave the uncorrected para/ortho ratios of Table 3. The standard deviation error estimates include an allowance for calibration and pointing uncertainties. The DR21 (OH) value as observed with the 20-m dish is marginally higher than with the 7-m antenna: 0.65±0.08, compared with 0.50±0.05. The Orion profile seems to be double, with peaks at 8 and 10 km s^{-1}. This agrees with the suggestion of Bastien et al. (1985) that two clouds are present at these radial velocities. However, the H_2CO profiles do not show such a well-defined structure.

Up to this point we have ignored possible contamination of the $3_{03}-2_{02}$ line by inclusion of the $3_{22}-2_{21}$ transition, which is only 0.55±0.1 MHz (1.6±0.3 km s^{-1}) away (see Table 1). The intensity of the latter should approximately equal that of the other $K_a=2$ transition, the nearby $3_{21}-2_{20}$ (frequency 11.40±0.1 MHz higher than the $3_{03}-2_{02}$ line). The $3_{21}-2_{20}$ line was outside the range covered by the 100 kHz filter bank but *was* observed in the 250 kHz filter bank spectra with an intensity relative to the $3_{03}-2_{02}$ line of 0.16±0.02 in Orion-KL and 0.14±0.03 in DR21 (OH). The para-

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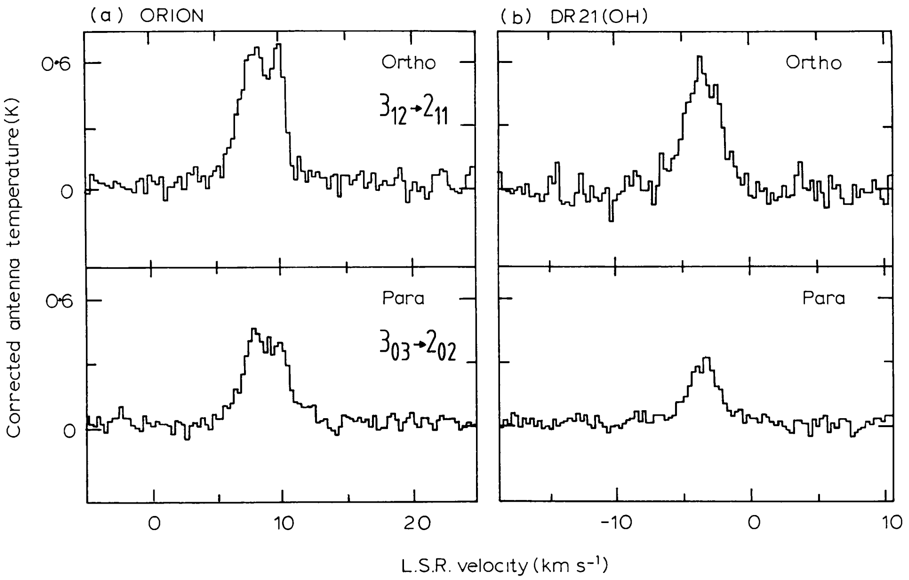

Fig. 1a and b. Spectra of ortho (104 GHz) and para (103 GHz) H_2CS towards **a** Orion and **b** DR21 (OH) with a 105″ beam and a resolution of 100 kHz (~0.3 km s^{-1}), using the Bell Labs. 7-m telescope

to-ortho-line ratios should therefore be corrected to 0.51 ± 0.04 in Orion and 0.44 ± 0.05 in DR21 (OH). Applying this correction, the para/ortho ratio for DR21 (OH) for Onsala should be reduced to 0.56 ± 0.08.

At Onsala, observations of the $3_{13}-2_{12}$ line of ortho-$H_2C^{34}S$ were made towards Orion-KL. There was no published rest frequency, and it was necessary to estimate it from the limited isotopic data provided by Johnson et al. (1972). The estimate was 99772 ± 1 MHz. The spectrum observed revealed only one feature within ± 3 MHz of this value. If this feature is accepted at $H_2C^{34}S$, then the best fit of the ^{32}S and ^{34}S lines occurred when the isotopic line frequency was taken to be 99773.4 MHz; the corresponding intensity ratio $H_2C^{32}S/H_2C^{34}S$ was 14^{+5}_{-3}. Subsequently, F. J. Lovas, on the basis of new measurements, has determined a line rest frequency of 99774.15 ± 0.05 MHz.

It was found that the velocities for the two ortho lines at 104 and 101 GHz which were measured at Onsala agreed best if a relative shift of their rest frequencies of 0.20 ± 0.02 MHz was made. This is approximately the same as the difference between the separation of the two observed and the two calculated frequencies in Table 1. Since the error in the two observed frequencies given by Johnson et al. (1972) were 0.07 and 0.12 MHz for the 104 and 101 GHz lines respectively, we judge that the former rest frequency should be decreased by 0.07 MHz and the latter increased by 0.13 MHz. As described earlier, the 103–104 GHz frequency difference was determined by line fitting and accordingly the 103 GHz rest frequency was increased by 0.14 (0.21–0.07) MHz. The three values are given in Table 1, together with that of the ^{34}S line.

Discussion and conclusions

Large velocity gradient (LVG) Sobolev models incorporating spherical geometry and predominantly collisional excitation have been commonly used to derive densities and abundances for H_2CO. For Orion, Bastien et al. (1984) have fitted observations of a number of transitions by a model based on collisional excitation rates calculated by Green et al. (1978). As no collision rates are available for H_2CS, we have taken the de-excitation rates to be the same as those of H_2CO for similar transitions. We would not expect such a procedure to yield correct excitation temperatures for the K-doublets (where refrigeration etc. depends markedly on the properties of the individual molecule), but it should give reasonable estimates for rotational transitions between doublet pairs (i.e., $\Delta J = \pm 1$). The model, discussed by Shukre and Rees (1984), provides for the inclusion of IR and free-free radiation, but as used in the present instance is essentially the same as the model for H_2CO developed and described in detail by Henkel et al. (1980). The energy levels included the 18 lowest levels (with 25 transitions) for ortho H_2CS and 23 levels (with 26 levels for para H_2CS.

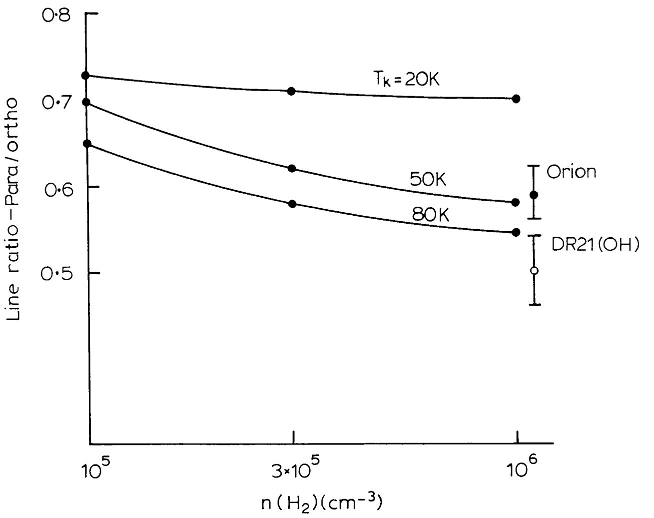

Fig. 2. Model calculations of the ratio of the intensities of the para $3_{03}-2_{02}$ (103 GHz) and ortho $3_{12}-2_{11}$ (104 GHz) transitions as a function of hydrogen density $n(H_2)$ for three values of kinetic temperature T_k assuming a true para/ortho ratio of 1/3 and abundance ratio $X = [H_2CS]/[H_2] = 10^{-11}$. The filled circle refers to the Bell Labs. result for Orion. The open circles refer to DR21 (OH). The higher value refers to the Onsala data, and the lower to a ratio obtained from Bell Labs. measurements

Figure 2 shows the calculated para/ortho (104 GHz) line intensity ratio for a range of densities and temperatures assuming the canonical para/ortho abundance ratio of 1 : 3. We have taken $X(dV/dr)^{-1} = 10^{-11}$, i.e., for a gradient $dV/dr = 1$ km s^{-1} pc^{-1}, the

Table 4. Ratios of $(3_{21}-2_{20})$ and $(3_{03}-2_{02})$ intensities and derived kinetic temperatures

Source	7-m Bell Labs.		20-m Onsala	
	Line Ratio	Kinetic Temp	Line Ratio	Kinetic Temp.
Orion	0.16 ± 0.02	45 ± 5	0.10 ± 0.05	33 ± 10
DR21 (OH)	0.14 ± 0.03	41 ± 6	0.15 ± 0.07	44 ± 15

relative abundance $X = [H_2CS]/[H_2] = 10^{-11}$. There is a slight increase in the line ratio with X; for $n(H_2) = 10^6$ and $T_k = 70$ K, usually considered appropriate to H_2CO in Orion, the ratio increases from 0.55 to 0.59 as X increases from 10^{-11} to 10^{-10}, although over the same range the 104 GHz line intensity and optical depth would increase almost linearly with X. We note that the para/ortho line intensities are not very different from the LTE values which apply in the limit of very large H_2 densities. The LTE values are 0.64 ($T_K = 20$ K), 0.57 ($T_K = 30$ K), 0.49 ($T_K = 50$ K), and 0.46 ($T_K = 70$ K).

It can be seen from Fig. 2 that the Orion value agrees within the error limits with the calculated value of 0.55 for a para/ortho ratio of 1 : 3. The data for DR21 (OH) suggests a value of ~20% lower. The discrepancy is reduced if a weighted average of 0.48 ± 0.05 is taken for the two determinations in Table 3. However, we cannot exclude the possibility of the intensity ratio being higher for the Onsala observations (from the smaller beam). This might occur if the contamination of the para line by the $3_{22}-2_{21}$ contribution were larger as might arise if DR21 (OH) contains a hot dense core, as postulated by Wilson et al. (1982) to account for the distribution of 2 cm H_2CO emission (core diameter $\leqq 0\farcm5$). Information on kinetic temperature in the H_2CS clouds may be obtained from the ratio of the $(3_{21}-2_{20})$ and $(3_{03}-2_{02})$ lines.

Because the H_2CS molecules is such a good approximation to a prolate symmetrical top (asymmetry parameter $\kappa = -0.992$) the populations of the lower $K_a = 2$ levels are controlled by collisions if $n(H_2) > \sim 10^3\,\mathrm{cm}^{-3}$. Thus, independently of the model, the intensity ratio $I(3_{22}-2_{21})/I(3_{03}-2_{02})$ should be $\sim 0.55 \exp(-56/T_K)$ (where 0.55 is the line strength ratio, and the energy separation of the 2_{21} and 2_{02} levels is 56 K). The line ratios and derived kinetic temperatures are shown in Table 4. For the larger beam results, T_K takes the values 45 ± 5 K and 41 ± 6 K for Orion and DR21 (OH) respectively. The values with the smaller beam are not significantly higher and so there is no evidence in our data for hot cores. The derived kinetic temperatures are somewhat lower than the usually accepted values of 70 and 50 K for the two sources. This might be obtained as a result of radiative coupling between the $K_a = 0$ and $K_a = 2$ ladders, because of partial overlapping of the $3_{22}-2_{21}$ and $3_{03}-2_{02}$ lines (the rest frequencies are 0.55 MHz or $1.6\,\mathrm{km\,s}^{-1}$ apart). We would not except such an effect to be very important at the high densities applying in the two sources. It has been ignored in the corrections to the para/ortho ratios made in Table 3.

If we assume that the kinetic temperatures agree and that the abundance ratios of H_2CS and H_2CO are constant through a molecular cloud, then this ratio may be derived from the model calculations. For H_2CO Bastien et al. (1984) derive $X \approx 10^{-9}$ for the central core in Orion. For H_2CS the central radiation intensity of the ortho lines is ~6 K for a source size of $0\farcm5$ and the corresponding abundance from the model fitting is $4.5\,10^{-11}$. On this basis $[H_2CO] : [H_2CS] \approx 22$, which is somewhat smaller than the cosmic [O] : [S] ratio of 40, but similar to the result Gardner et al. (1980) obtained for a sample of 10 sources (not including Orion). For $X = 4.5\,10^{-11}$ the optical depth of the ortho lines is ~0.1 and any corrections to the isotope $[H_2CS] : [H_2C^{34}S]$ ratio for optical depth should not exceed 5–10%. Thus the corrected ratio 15^{+5}_{-3} is not significantly different from the terrestrial value of 22.

In conclusion any departures of the para/ortho ratio from the usually assumed value of 1/3 are small, and within the range of uncertainty of the observations and modelling. In the case of H_2CO, Kahane et al. (1984) have deduced that a para/ortho ratio of 1/3 would result if H_2CO were destroyed by a reaction with H_3^+ at a temperature >15 K and formed by a recombination of H_3CO^+ with an electron. It is not clear from the discussion of Prasad and Huntress (1982) that similar reactions would be important for H_2CS, if ion-molecule reactions are the dominant feature of the chemistry.

It would be useful to have the results for a larger source sample, which should include some sources with lower densities, temperatures and linewidths than Orion and DR21 (OH), particularly when calculated collision rates become available. The effects of radiative coupling between the $K_a = 0$ and $K_a = 2$ ladders should be investigated. Observations of other transitions of para-H_2CS such as the 4–3 lines at 137 GHz might shed light on this matter. Improvements in sensitivity and laboratory frequencies are necessary to warrant further isotopic studies, although it would be of interest to compare them with measurements of CS (Frerking et al., 1980). Because of the lower abundance of H_2CS we could be sure that optical depth and radiation trapping effects are smaller than for CS and so derived isotopic abundances would be more reliable.

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References

Bastien, P., Batrla, W., Henkel, C., Walmsley, C.M., Wilson, T.L.: 1984, *Astron. Astrophys.* (in press)

Frerking, M.A., Wilson, R.W., Linke, R.A., Wannier, P.G.: 1980, *Astrophys. J.* **240**, 65

Gardner, F.F., Höglund, B., Whiteoak, J.B.: 1980, *Monthly Notices Roy. Astron. Soc.* **191**, 19P

Green, S., Garrison, B.J., Lester, W.A., Miller, W.H.: 1978, *Astrophys. J. Suppl. Ser.* **37**, 321

Henkel, C., Walmsley, C.M., Wilson, T.L.: 1980, *Astron. Astrophys.* **82**, 41

Johnson, D.R., Lovas, F.J., Kirchoff, W.J.: 1972, *J. Phys. Chem. Data* **1**, 1011

Kahane, C., Frerking, M., Langer, W., Encrenaz, P., Lucas, R.: 1984, *Astron. Astrophys.* **137**, 211

Liszt, H.S.: 1978, *Astrophys. J.* **219**, 454

Prasad, S.S., Huntress, W.T.: 1982, *Astrophys. J.* **260**, 590

Shukre, C., Rees, D.E.: 1984 (in preparation)

Wilson, T.L., Martin-Pintado, J., Gardner, F.F., Henkel, C.: 1982, *Astron. Astrophys.* **107**, L10