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THREE NEW "NONTERRESTRIAL" MOLECULES

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ABSTRACT

Eight new interstellar lines have been detected from three molecules not previously observed spectroscopically in space or in the laboratory. One is a linear or nearly linear molecule with microwave constants $B_0 = 21{,}337.15 \pm 0.06$ MHz, $D_0 = 21.4 \pm 1.5$ kHz. This is the thioformyl ion HCS^+, first identified because B_0 and D_0 are close to those calculated, and now confirmed by laboratory detection of one of our lines (Gudeman *et al.*). The second molecule, also linear or nearly so, has microwave constants $B_0 = 10{,}691.406 \pm 0.043$ MHz, $D_0 = 1.84 \pm 0.91$ kHz close to those expected for the isoelectronic systems $HOCO^+$ and HOCN; a choice between the two cannot be made on the basis of the available astronomical data. The existence of a third molecule is deduced from an unidentified line at 85,338 MHz that has been found in many sources, is fairly intense in several, and may be self-absorbed in Sgr B2. No hfs or harmonically related lines to reveal the identity of this molecule have been detected.

Subject headings: interstellar: molecules

I. INTRODUCTION

Most interstellar molecules are stable compounds found in any chemical stockroom, but nearly one-fifth are highly reactive ions, radicals, and acetylenic carbon chains so unfamiliar in the terrestrial laboratory that radio astronomers and chemists have dubbed them "nonterrestrial." We assumed that we had found another molecule of this kind when we detected several years ago a triplet of interstellar lines at 85 GHz (Fig. 1) failing to match the spectrum of any known molecule. A long series of subsequent observations, however, has shown that this assumption was not entirely correct. The lines are indeed "nonterrestrial," as far as we can tell from an exhaustive survey of the spectra of known molecules, but the triplet is fake, being produced by not one but three new molecules.

The first evidence against a single molecule was observation of source-to-source variation in relative intensities, an effect that is most pronounced for the high-frequency component C in Figure 1. This line has been detected only in Sgr B2, but the close low-frequency pair AB has been found in a number of additional sources, in three of which (Ori A, DR 21, and TMC-1) its intensity rivals or exceeds that in Sgr B2. Molecular excitation fails to explain this variation, for it is generally lower in Sgr B2 than in Ori A and DR 21, and hence C is unlikely to be a high-lying transition related to AB, for example a vibrational or torsional satellite. The most plausible explanation is that C is simply another molecule.

The AB doublet itself is a more subtle problem that misled us for several years. In many sources the intensity of B relative to A is close to that in Figure 1, and in both Sgr B2 and Ori A it is quite constant along a north-south strip over 6′ long. Only when we found that B is weak by a factor of over 2 in W3 (OH) did we conclude that this structure too was probably fortuitous.

Proof that we were dealing with three molecules, and clues to the identity of two, finally came when we detected well away in the millimeter-wave spectrum of Ori A and Sgr B2 lines harmonically related to B and C. We had tried from the start to find lines at 1/2, 5/4, 4/3, and other simple rational fractions of the triplet frequency, since such harmonic relations have been instrumental in identifying other nonterrestrial lines, but progress was slow because many receiver changes were required, and the sensitivity at certain frequencies was poor. During five observing runs on the 36 foot (10.9 m) telescope and the 5 m telescope of the University of Texas, over a 3 yr period, no harmonically related lines were detected.

In the winter of 1980, however, we took up the search with the Bell 7 m telescope and its very sensitive 100–150 GHz cryogenic receiver and soon found a line in Ori A at almost exactly 3/2B. Subsequently in Sgr B2 we

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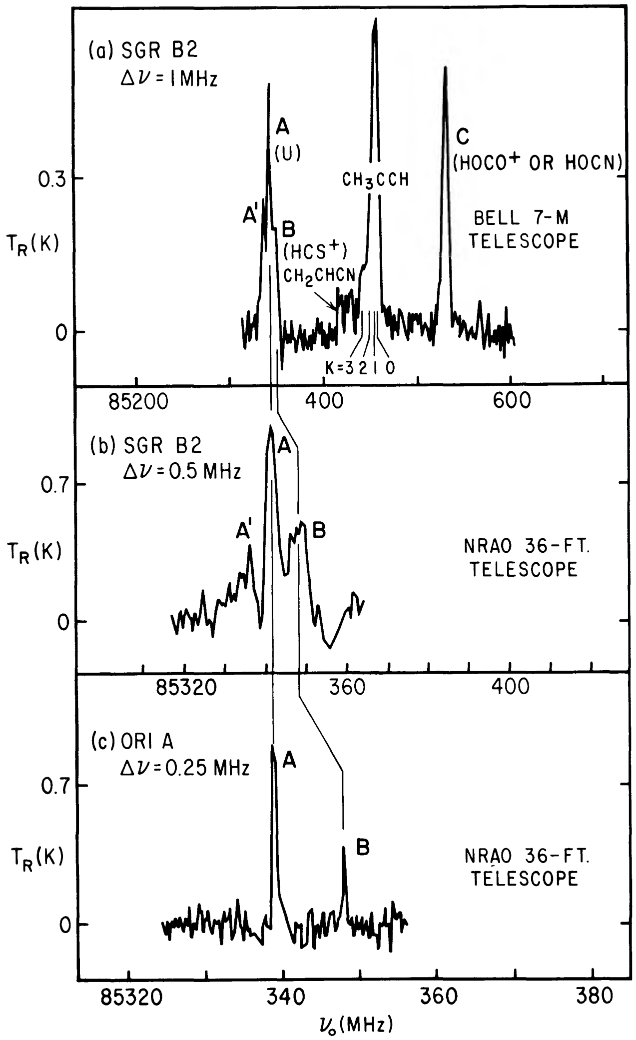

FIG. 1.—The fortuitous triplet ABC of "nonterrestrial" interstellar lines at 85 GHz. (*a*) The triplet in Sgr B2 (OH), flanking the strong known $J=5\rightarrow4$ transitions of methylacetylene. Here the two lower-frequency components A and B are blended; but at twice the resolution, in (*b*), the two are distinctly resolved, and there is a possible additional line A′. Evidence that A′ is merely a high-velocity component of A peculiar to Sgr B2, not a satellite transition, is provided by (*c*), a high-resolution spectrum 1′ E, 3′ N of KL in the Orion Nebula, where A′ is absent. The double velocity structure of A in Sgr B2, peaking at 52 and 75 km s^{-1}, closely resembles the self-absorbed line structure of $H^{13}CO^+$ and other light molecules, suggesting that the unknown carrier of A may also be a fairly simple compound. The intensity scale T_R here and in Figs. 2 and 3 is antenna temperature corrected for atmospheric absorption and beam efficiency; ν_0 is calculated for $v_{LSR} =$ 62 km s^{-1} in Sgr B2 and 9 km s^{-1} in Ori A.

detected other lines at 5/4C and 3/2C. Finally, when a new receiver working above 200 GHz was installed on the telescope, we returned to Ori A and succeeded in detecting lines at 5/2B and 3B. With this highly specific data it has been possible to deduce with remarkable precision the mass and structure of the two molecules producing B and C.

II. HCS^+

Line B and three lines toward the Kleinmann-Low Nebula harmonically related to it are shown in Figure 2; rest frequencies, found by assuming that the radial velocity is the same as that of other molecules in this source, are given in Table 1. As the third column of

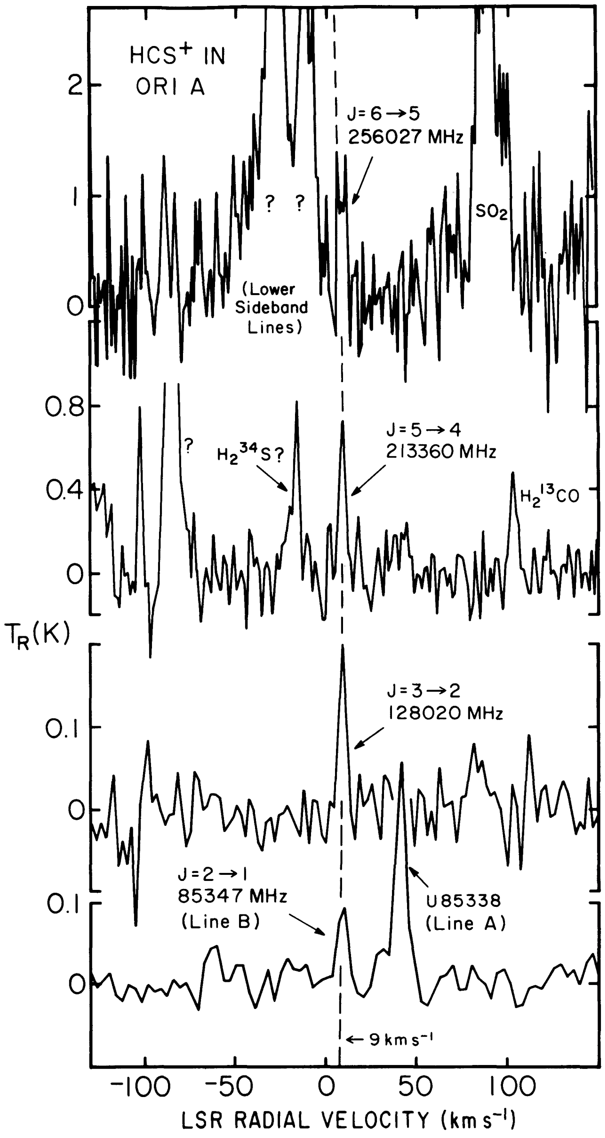

FIG. 2.—Four harmonically related lines in the Orion Nebula of the HCS^+ ion, observed at a spectral resolution of 1 MHz. Radial velocities are not assumed to be 9.0 km s^{-1} (as in Table 1), but are calculated from the B_0 and D_0 in Table 2, to demonstrate how closely four observed lines are fitted by two free parameters. Relative intensities also support the assignment: they are those expected for optically thin lines of a linear molecule at a rotation temperature of 70 K or more.

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TABLE 1

NEW INTERSTELLAR LINES IDENTIFIED AS HCS^+

Transition $J' \rightarrow J''$	Rest Frequency ν_0 (MHz)	$\nu_0 - \nu_{\mathrm{har}}$ (MHz)	$\nu_0 - \nu_{\mathrm{calc}}$ (MHz)
2→1......	85,347.90±0.38	0	−0.01
3→2......	128,020.67±0.30	−1.18	+0.08
5→4......	213,360.53±0.58	−9.22	−0.27
6→5......	256,027.8 ±1.0	−15.90	+0.49

NOTE.—Rest frequencies were obtained by fitting Gaussian profiles to the Ori A data in Fig. 2, on the assumption that the radial velocity in the local standard of rest is 9.0 km s^{-1}, the velocity of most other molecules in this source. Uncertainties are 1 σ. The third column is the deviation from strict harmonicity with respect to the 2→1 transition: $\nu_{\mathrm{har}} = (J'/2)\nu_0(2 \rightarrow 1)$. The last column is the residual of the fit to the nonrigid rotor, eq. (1).

Table 1 shows, harmonicity, while extremely close, is not exact, but the deviation is just that of a nonrigid linear or nearly linear molecule subject to centrifugal distortion with rotational frequencies

$$\nu(J+1 \rightarrow J) = 2B_0(J+1) - 4D_0(J+1)^3. \qquad (1)$$

A least-squares fit of equation (1) to the frequencies in Table 1 yields the "interstellar" rotation constant B_0 and centrifugal distortion constant D_0 in Table 2. Residuals of the fit (last column of Table 1) are small—less than one spectrometer channel (1 MHz) for each line. A search for lines halfway between 2→1 and 3→2, one-third the way between, etc., has eliminated the possibility that B_0 is a submultiple of the value in Table 2.

As Table 2 shows, these microwave constants are very close to those expected for the thioformyl ion HCS^+. As HCS^+ is an extremely plausible—even necessary—constituent of the interstellar gas, and as no other hypothetical molecule could be found to match the astronomical data, we concluded that this was almost certainly the molecule we had found (Thaddeus 1980). Conclusive laboratory confirmation of this identification is reported by Gudeman *et al.* (1981) in the following *Letter*.

In a preliminary survey of HCS^+ we have detected the 2→1 or 3→2 transition in 10 standard sources and partially mapped its distribution in two: Sgr B2 and Ori A. The intensity of HCS^+ correlates well with that of CS, one of its likely progenitors, but relative to CS the abundance of HCS^+ is surprisingly large. We find the column density ratio HCS^+/CS to be typically $1-3 \times 10^{-2}$, not 1×10^{-3} as predicted by Mitchell, Ginsburg, and Kuntz (1978) and McAllister (1978), suggesting that data on HCS^+ may provide an important constraint on molecular formation in space.

TABLE 2

MICROWAVE CONSTANTS OF HCS^+

Determination	B_0(MHz)	D_0(kHz)
Interstellar	21,337.15±0.06	21.4±1.5
Theoretical	21,558±216[a]	21.2±0.1[b]

[a] *Ab initio* calculation (Wilson 1978).

[b] Lab value for HCP (Johns, Stone, and Winnewisser 1971).

III. $HOCO^+$ OR HOCN

Line C and the two higher-frequency lines harmonically related to it that we have detected in Sgr B2 are shown in Figure 3; rest frequencies and microwave constants derived as for HCS^+ are given in Tables 3 and 4. Harmonicity is here extremely close, and, as a comparison of columns 3 and 4 in Table 3 shows, the data are quite well fitted with $D_0 = 0$. The ambiguity in B_0 has again been eliminated by a search for intermediate lines, and it is virtually certain that those shown in Figure 3 are, as assigned, successive rotational transitions.

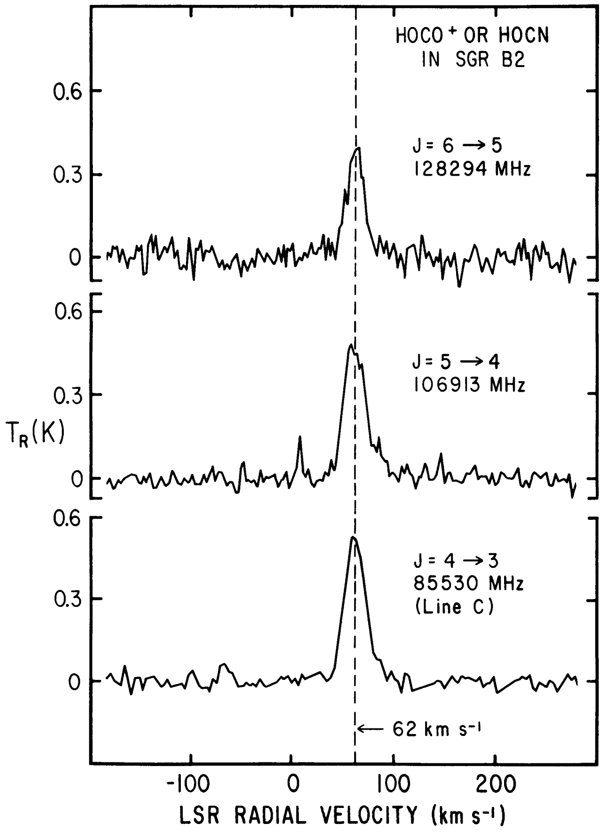

FIG. 3.—Harmonically related lines in Sgr B2 (OH) attributed to either $HOCO^+$ or HOCN, observed at a spectral resolution of 1 MHz. Radial velocities are calculated from the microwave constants in Table 4. Relative intensities are those expected for optically thin lines of a nearly linear molecule at a rotational temperature of 8.7±0.8 K.

TABLE 3

NEW LINES IN SAGITTARIUS B2 IDENTIFIED AS HOCO$^+$ OR HOCN

Transition ($J' \rightarrow J''$)	Rest Frequency ν_0 (MHz)	$\nu_0 - \nu_{\rm har}$ (MHz)	$\nu_0 - \nu_{\rm calc}$ (MHz)
4→3......	85,530.68±0.15	0	−0.10
5→4......	106,913.36±0.19	+0.01	+0.22
6→5......	128,294.89±0.41	−1.13	−0.39

NOTE.—Rest frequencies were obtained by fitting Gaussian profiles to the Ori A data in Fig. 2, on the assumption that the radial velocity in the local standard of rest is 9.0 km s^{-1}, the velocity of most other molecules in this source. Uncertainties are 1 σ. The third column is the deviation from strict harmonicity with respect to the $2 \rightarrow 1$ transition: $\nu_{\rm har} = (J'/2)\nu_0(2 \rightarrow 1)$. The last column is the residual of the fit to the nonrigid rotor, eq. (1).

The rotation constant of a molecule with a linear or nearly linear heavy atom backbone of three second-row atoms is expected to lie near 10 GHz, just as now required. There are at least 100 molecules of this formula that can be constructed by permuting C, N, and O if no restrictions other than the requirement of a stable bond are placed on the addition of H atoms. Only terminal H atoms are permissible, however, for otherwise the backbone would be bent, and there are not likely to be more than one H at either end, for otherwise satellite rotational structure would probably appear that is not observed. Elsewhere in the spectrum of Sgr B2, close satellites with $K = 1$, 2, and 3 are observed for CH_3CN and CH_3CCH (cf. Fig. 1*a*), and more distant but intense $K = 1$ (ortho) satellites are seen for H_2CO and H_2CCO. Such satellites of the lines in Figure 3 are not likely to have escaped detection.

Thus the structural formula for the molecule or ion in question is likely to be *XYZ*, *HXYZ*, or *HXYZH*, where $X, Y, Z =$ C,N, or O. There are nine polar permutations of the first structure with an even number of electrons, 27 of the second, and nine of the third, for a total of 45 possibilities. Some of these, however, are known molecules (e.g., CCO, HCNO, and HCOOH), others have bent backbones according to the Walsh rules, some thought to be linear have been shown by *ab initio* calculations to possess rotation constants that differ significantly from 10.6 GHz (e.g., CCN$^+$ and HCCC$^+$), and yet others are implausible, being excited isomers or protonated derivatives of molecules not observed in space—or molecules with one or more NO bonds, a bond seldom encountered in interstellar chemistry.

When these are set aside, there remain only two molecules, protonated carbon dioxide HOCO$^+$ and cyanic acid HOCN, and there is little evidence of either an empirical or theoretical character that inclines us to prefer one to the other. The two are isoelectronic; both are thought to have a nearly linear backbone, and both according to *ab initio* calculations have a rotation constant that agrees nicely with that of our second new molecule (Table 4). Neither is implausible from an astrochemical standpoint: HOCO$^+$ is readily formed by $CO_2 + H_3^+ \rightarrow HOCO^+ + H_2$ and other reactions (and for this reason has already been sought in interstellar clouds: Herbst *et al.* 1977); HOCN is an isomer of isocyanic acid HNCO, a stable molecule fairly abundant in Sgr B2.

Both HOCO$^+$ and HOCN possess $K = \pm 1$ rotational satellites several hundred MHz to either side of the lines in Figure 3, but owing to the absence of ortho-para symmetry, these will be much weaker than the $K = \pm 1$ lines of H_2CO and H_2CCO, at least in a fairly cold source like Sgr B2. By analogy with HNCO, for which the intensity ratio $K = 1/K = 0 \approx 0.03$ for $J = 4 \rightarrow 3$ in Sgr B2, we expect the satellite intensity to be only ~0.01 K, or somewhat below our level of detection. For the $J = 4 \rightarrow 3$ line, we have attempted to find these satellites, but failed.

There is a potentially crucial astronomical test of HOCO$^+$ versus HOCN: detection of the quadrupole hyperfine structure of the N nucleus in HOCN. Such hfs rapidly collapses with increasing *J* and is expected for the lines in Figure 3 to be negligible; in Sgr B2, however, it should be detectable for the $J = 1 \rightarrow 0$ transition at 21,383.8 MHz, if the HOCN hyperfine interaction is comparable to that of other molecules with a terminal nitrogen (e.g., HCN). An attempt by Dr. P. C. Myers to carry out this test on the 37 m Haystack telescope has unfortunately failed. The expected antenna temperature of the line *without hyperfine dilution* is only ~0.01 K,

TABLE 4

MICROWAVE CONSTANTS OF THE SECOND NEW MOLECULE IN SAGITTARIUS B2 VERSUS THOSE EXPECTED FOR HOCO$^+$ AND HOCN

Molecule	B_0(MHz)	D_0(kHz)
New molecule	10,691.406±0.043	1.84±0.91
HOCO$^+$...........	10,740±100[a]	3.5±0.5[b]
HOCN	10,555±120[c]	3.5±0.5[b]

[a] *Ab initio* calculation (Green *et al.* 1976).

[b] Lab value for HNCO (Kewley, Sastry, and Winnewisser 1963).

[c] *Ab initio* calculation (McLean, Loew, and Berkowitz 1977).

and owing in part to contamination by H67α at 21,384.8 MHz, it proved impossible in an 8 hr integration to detect the line at all, much less determine whether hfs was present. A better source for our new molecule than Sgr B2 is probably required for this test to succeed.

IV. U85338

Stripped of its decoys, one might think that the intense A component of our triplet would be easy to interpret, but it has defied all attempts at identification. Our observations, however, provide a number of clues as to the nature of its carrier:

1. It is probably a fairly simple and strongly polar molecule, and A is likely to be a low-lying transition, for A has been found in nearly every source surveyed (10 out of 11), is apparently self-reversed in Sgr B2 (OH) (Fig. 1*b*), and is appreciably extended in Ori A, Sgr B2, and TMC-1. At the best position in TMC-1, A is quite intense ($T_R = 3.1$ K) and remarkably narrow (0.53 km s^{-1}), yielding a precise value for the rest frequency: 85,338.85 ± 0.05 MHz.

2. It is probably not a linear molecule with a $^1\Sigma$ or $^2\Sigma$ ground state, for we have failed to detect lines at or near 1/2, 12/11, 10/9, 9/8, 8/7, 7/6, 6/5, 5/4, 4/3, 2, or 3 times ν_0 in Ori A or Sgr B2. Furthermore, the absence of hfs or λ-doubling near A itself rules out most plausible linear molecules with orbital angular momentum in the ground state. Linear molecules with a $^3\Sigma$ ground state and large spin splittings (like SO) remain a possibility.

3. It is not likely (*a*) to be an ion, or (*b*) to contain oxygen, for A is found in the oxygen-deficient source IRC +10216, where no ion has been observed. We are uncertain, however, how much weight to give this rule, partly because it is so restrictive, and have often disregarded it when considering candidates for U85338.

The long list of hypothetical molecules we have scrutinized includes triplet species such as HCCN, excited isomers of known interstellar molecules such as H_2CC, simple ions violating rule 3(*b*) such as CCH^+, and asymmetric molecules with *b*-type transitions such as cyclopropenylidene C_3H_2. All have been rejected, however, for various reasons, and the identity of U85338 remains an intriguing puzzle in molecular radio astronomy.

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