

Microwave Spectrum and Conformation of Glycine

By RONALD D. BROWN*, PETER D. GODFREY, JOHN W. V. STOREY, and MARIE-PAULE BASSEZ
(Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia)

Summary The microwave spectrum of glycine vapour has been measured and analysed; it is in the molecular form with a dipole moment of 4.5–4.6 D and probably having conformation (4), which is in conflict with a recent theoretical study that implies that conformation (3) is more stable.

BECAUSE of its pivotal biological significance as the simplest amino acid there is considerable interest in the structure and other properties of the glycine molecule. Although X-ray and neutron diffraction studies of the glycine crystal have been reported¹ revealing bond lengths, angles, and packing arrangements in the crystal, it is of great importance to have information about an isolated glycine molecule. This would make solid-state effects apparent, not only in relation to intermolecular hydrogen bonding but also because glycine exists as the zwitterion in the solid state, whereas it is expected that it might be in the less polar molecular form when isolated as a gaseous molecule. However the study of the rotational spectrum of glycine vapour has presented considerable difficulties because of the relatively low volatility coupled with its thermal instability. In the last few years there has been a further stimulus to endeavouring to study the rotational spectrum of the molecule because of the possibility of detecting interstellar glycine.

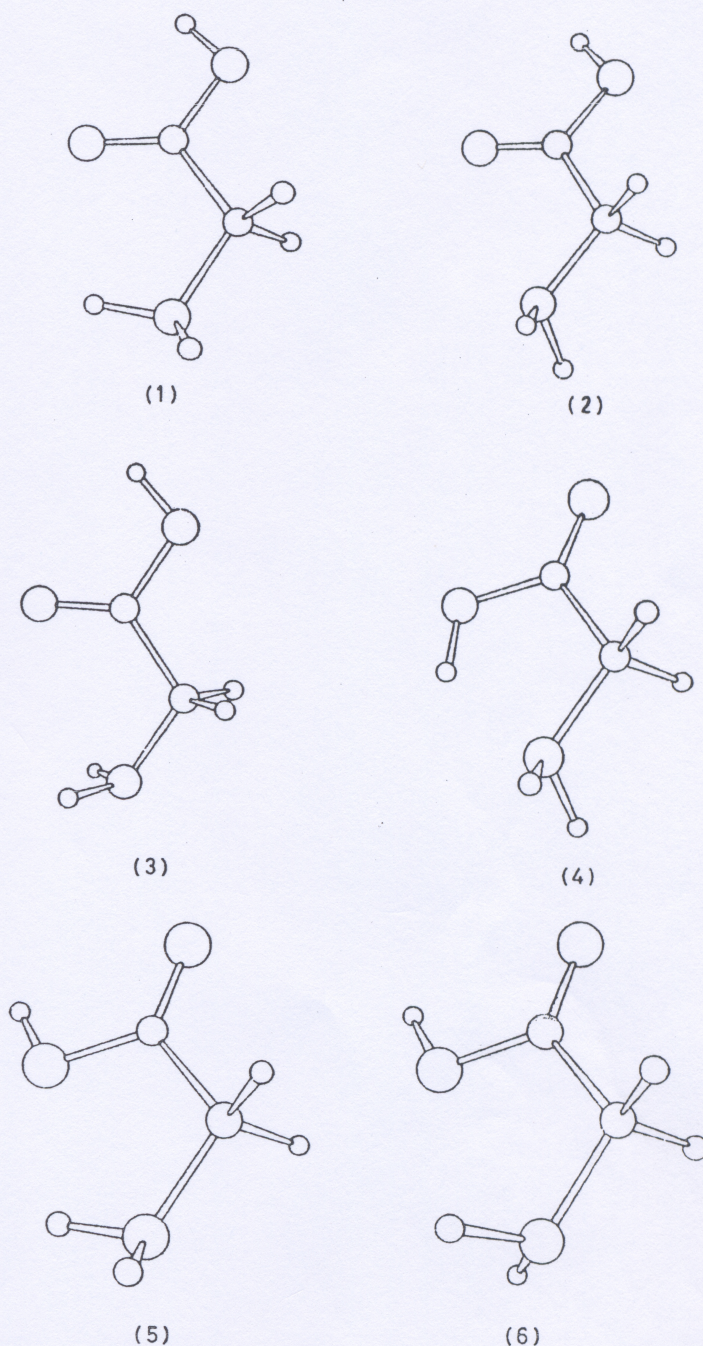
TABLE 1. Some of the measured microwave transition (MHz) attributed to glycine

$7_{16} \leftarrow 6_{15}$	51027.4	$4_{22} \leftarrow 3_{21}$	29398.6
$8_{17} \leftarrow 7_{16}$	57341.0	$4_{23} \leftarrow 3_{22}$	28215.6
$8_{18} \leftarrow 7_{17}$	560757.3	$8_{35} \rightarrow 7_{34}$	59137.0

We have now succeeded in detecting the microwave spectrum of glycine in a specially constructed cell designed to maintain it at a temperature at which it has an appreciable vapour pressure (160–200 °C) while minimising effects of decomposition. It consisted of a large, uniformly heated, stainless steel vacuum tank fitted with parallel plates to conduct the microwaves through the vapour and to enable Stark-modulation of signals to be employed.

More than 200 lines attributable to glycine have been measured in the frequency range 35–63 GHz. It proved possible to assign many of the lines as *a*-type transitions in the spectrum of an almost rigid rotor with the following values of the spectral parameters: $A = 10129.200$, $B = 4071.449$, $C = 3007.511$, $D_J = 0.00052$, and $D_{JK} = 0.00548$ MHz. The frequencies of some of the assigned lines are given in Table 1. In addition, by measuring the Stark effect on the $4_{23} \leftarrow 3_{22}$ transition we have obtained a value of 4.5 D (1.3×10^{-29} C m) for the component of the molecular dipole moment along the *a* inertial axis. We were unable to detect any *b*-type transitions and estimate that $\mu_b < 1$ D. Thus the molecular dipole moment is 4.5–4.6 D.

While we cannot deduce the molecular geometry from just the set of rotational constants for a single isotopic species of glycine, we can compare our results with values of the constants calculated for various plausible conformations



FIGURE

of the molecule. The various conformations are shown in the Figure and the predicted rotational constants and dipole moment components are listed in Table 2. Geometries were estimated by combining data for propionic acid² and methylamine.³ The dipole components were computed by using the simple but reasonably reliable assumption that dipole moments can be predominantly attributed to lone pair electrons and using the values of 1.70, 2.35, and 1.31 D for the hydroxy oxygen, carbonyl oxygen, and amino

nitrogen, respectively. We did not seriously consider zwitterion structures because they would imply very much greater values of the dipole moment than that observed.

TABLE 2. Rotational constants and dipole moment components of glycine conformations

Conformation	A^a	B^a	C^a	μ_a^b	μ_b^b	μ_c^b
(1)	10.45	3.88	2.91	0.3	0.1	1.1
(2)	10.06	3.76	2.87	0.2	1.9	0.0
(3)	10.36	3.90	2.93	1.0	0.2	0.0
(4)	10.47	4.03	3.01	3.5	1.7	0.0
(5)	10.21	4.12	3.02	0.1	0.6	1.1
(6)	10.11	4.15	3.05	0.6	0.8	0.0
Exp. values	10.13	4.07	3.01	4.5	≤ 1.0	0.0

^a In GHz. ^b In D.

Uncertainties in the predicted rotational constants are too great to enable a reliable choice to be made from them alone but the predicted dipole components of conformation (4) are most in harmony with our observations. Moreover for

this conformation alone one expects some of the rotational transitions to be readily modulated at very low voltages. It was this observation that helped in the initial stages of the assignment of the spectrum. An alternative configuration (3) has been predicted to be more stable than (4) on the basis of restricted Hartree-Fock M.O. calculations⁴ but (3) is predicted by us to have too low a value of the dipole moment components to be compatible with our assigned spectrum. We have not so far identified any lines than can be attributed to this conformer of glycine. We would expect such lines to be weaker if present at all. However, it is possible that the vapour contains one or more of the other conformers whose lines have so far escaped detection because they are less intense and less easily moderated by the Stark fields attainable in our spectrometer.

We conclude that the most likely conformation of the glycine molecule in the vapour state is (4).

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A search for interstellar glycine

Ronald D. Brown, Peter D. Godfrey, John W. V. Storey[★]
and Marie-Paule Bassez *Department of Chemistry, Monash University,
Clayton, Victoria 3168, Australia*

Brian J. Robinson, Robert A. Batchelor and
M. Gerry McCulloch *CSIRO, Division of Radiophysics, Epping,
New South Wales 2121, Australia*

Olof E. H. Rydbeck and Åke G. Hjalmarson *Onsala Space
Observatory, S43034 Onsala, Sweden*

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Summary. A search has been made for the simplest amino acid – glycine – in Sgr B2, Ori A and seven other molecular clouds. Six different lines were sought ranging from 83.4 GHz down to 22.7 GHz and radiotelescopes at Parkes, New South Wales, Kitt Peak, Arizona, and Onsala, Sweden, were used. On the assumption of reasonable values for T_{ex} and Boltzmann distributions over rotational energy states, upper limits of column densities for glycine of a few times 10^{12} cm^{-2} to a few times 10^{14} cm^{-2} were typically established in the sources surveyed. Glycine appears to be less abundant than ethanol or ethyl cyanide in molecular clouds such as Sgr B2 and Ori A.

The recent achievement of the assignment of the microwave spectrum of the simplest amino acid (Brown *et al.* 1978) – glycine – has made it feasible to search for interstellar glycine in galactic molecular clouds such as Sgr B2 and Ori A. We have conducted a search in these and some other sources using radiotelescopes at the Australian National Radio-astronomical Observatory, Parkes, the Onsala Space Observatory and at Kitt Peak NRAO. (The National Radio Astronomy Observatory is operated by Associated Universities, Inc., under contract with the National Science Foundation.)

At Parkes the central 17 m of the 64-m dish was used at a frequency of 75 GHz with a cooled mixer receiver of DSB system temperature 340 K; at Onsala the 20-m millimetre-wave telescope was fitted with a maser receiver at 22 GHz of SSB system temperature 130 K and at Kitt Peak the 11-m millimetre-wave telescope was fitted with a cooled mixer receiver of SSB system temperature 1700 K at frequencies between 73 and 85 GHz.

[★] Present address: Department of Physics, University of California, Berkeley, California, USA.

Glycine has a considerable number of rotational spectral transitions in the regions covered by these receivers. Our strategy was to select those transitions for which: (a) the energy of the upper state is not too high, (b) the transition has a large Einstein A coefficient and (c) the transition is the fastest radiative exit channel from the upper level.

The transitions best satisfying these criteria are listed in Table 1.

Table 1. Lines selected for glycine search.

	Transition	Frequency (MHz)	A_{ul} (/s)	E_u/k^*
(1)	11(3, 8)–10(3, 7)	83 356.0	6.1×10^{-5}	26.2
(2)	11(2, 9)–10(2, 8)	81 438.8	5.8×10^{-5}	24.9
(3)	11(3, 9)–10(3, 8)	77 916.7	4.9×10^{-5}	25.5
(4)	10(3, 7)–9(3, 6)	75 379.5	4.4×10^{-5}	22.2
(5)	11(1, 10)–10(1, 9)	75 009.9	4.6×10^{-5}	23.0
(6)	3(1, 2)–2(1, 1)	22 747.1	1.1×10^{-6}	2.4

* Energy of upper state of transition expressed in K.

Since any interstellar molecular lines from glycine were expected to be very weak, substantial integration times were used in order to search deeply for them. Details of the searches are given in Table 2. If we assume that a signal of intensity twice the rms noise might just be perceived then, with the assumed values of ΔV listed, we can derive upper limits for the column density of glycine in the various sources (see Table 2). In this we assumed a Boltzmann distribution over the lower energy states corresponding to the excitation temperature, T_{ex} , for which the values listed in the table were adopted. It does not seem justifiable to attempt more elaborate modelling of the excitation conditions in the various sources in view of the uncertainties about the physical conditions prevailing in them. In any case, a simple LTE model of the present kind accounted within a factor of 2 for observed intensities of a considerable number of lines of the relatively large molecule ethyl cyanide in Ori A (Johnson *et al.* 1977).

We conclude that, in most of the listed sources, glycine, if present, has a column density no greater than a few times 10^{12} cm^{-2} to a few times 10^{14} cm^{-2} . A tighter limit is set for several cold clouds. In the case of Sgr B2 and Ori A, where most molecules have been found, this implies that if glycine is present it is less abundant than some of the recently detected relatively large molecules such as ethanol and ethyl cyanide.

Speculations on any connection between interstellar amino acids and the origin of life (Brown 1977; Hoyle & Wickramasinghe 1977) must await still deeper searches with radio-telescopes and will probably require still further advances in low-noise millimetre-wave receivers.

Acknowledgments

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Table 2. Upper limits of glycine column density.

Source	α (1950) h m s	δ (1950) ° ' "	Telescope	Line	Frequency resolution	On-source time (s)	ΔT_a (rms)	Source parameters T_{ex} (K) ΔV (km/s)	Upper limit nL (cm ⁻²)
Sgr B2 (OH)	17 44 11	-28 22 30	Kitt Peak	(1)	1 MHz	8160	0.02*	35 25	7×10^{13}
			Kitt Peak	(2)	1 MHz	6000	0.03*	35 25	9×10^{13}
			Kitt Peak	(3)	1 MHz	7440	0.03*	35 25	9×10^{13}
		-28 22 42	Parke	(4)	1 MHz	33 600	0.014	35 25	$3 \times 10^{14} \dagger$
			Parke	(5)	1 MHz	29 700	0.02	35 25	$2 \times 10^{14} \dagger$
Ori A (OH)		-28 22 30	Kitt Peak	(5)	1 MHz	12 720	0.02*	35 25	8×10^{13}
	5 32 47	-5 24 21	Kitt Peak	(1)	250 kHz	7200	0.03*	90 3	3×10^{13}
			Kitt Peak	(2)	250 kHz	9600	0.03*	90 3	3×10^{13}
			Kitt Peak	(3)	250 kHz	4800	0.04*	90 3	4×10^{13}
			Parke	(4)	250 kHz	9600	0.03	90 3	$2 \times 10^{14} \dagger$
			Kitt Peak	(5)	250 kHz	16 400	0.02*	90 3	3×10^{13}
			Kitt Peak	(6)	240 kHz	34 500	0.02*	90 3	2×10^{14}
			Onsala	(6)	240 kHz	28 500	0.02*	40 2.5	6×10^{13}
	DR21 (OH)	20 37 14	42 12 00	Onsala	(6)	120 kHz	10 600	7 0.5	2×10^{12}
	Heiles 2	4 38 39	25 35 00	Onsala	(6)	60 kHz	3800	40 3	4×10^{14}
NGC 2264	6 38 24	9 32 12	Onsala	(6)	240 kHz	15 700	45 15	4×10^{14}	
W51	19 21 27	14 24 30	Onsala	(6)	240 kHz	2900	40 5	4×10^{14}	
NGC 7538	23 11 37	61 11 48	Onsala	(6)	240 kHz	12 200	33 7	2×10^{14}	
W3 (OH)	2 23 17	61 39 00	Onsala	(6)	240 kHz	5000	7 0.5	3×10^{12}	
L134N	15 51 30	-2 43 31	Onsala	(6)	60 kHz				

* T_a corrected for telescope efficiency of 70 per cent (Kitt Peak) and 75 per cent (Onsala).

† Assumes telescope efficiency of 20 per cent.

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