Centrifugal Distortion Parameters of Fulminic Acid, HCNO, from the Millimeter-Wave Rotational Spectra *

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A newly designed millimeter-wave spectrometer has been employed for precise measurements of the millimeter-wave rotational spectrum of HCNO. Absorptions in several excited vibrational states as well as the ground state could be measured. The present paper presents the observed frequencies and molecular constants obtained for the ground state and the first excited state of ν_4 and of ν_5, the vibrational bending modes.

In a series of papers [1–3] WINNEWISSER and BODENSEH have reported the microwave spectrum of the linear molecule HCNO in various vibrational states. This communication represents the first report on work extending the measurements on HCNO into the millimeter-wave region of the electromagnetic spectrum.

A newly designed millimeter-wave spectrometer for fast data acquisition was employed in this investigation in order to conveniently measure transient species. The spectrometer and its operation are described in detail in Ref. [4]. It is briefly described as a video-type spectrometer using King-Gordy type frequency multipliers and detectors [5] and employing a free space absorption cell (length 240 cm, diameter 10 cm). On-line signal averaging is achieved using a PDP 8/I computer with interfacing units to link and to synchronize the computer and the spectrometer.

Precise measurements in the mm-wave range of the rotational spectrum of HCNO have been made from 40 to 280 GHz and some submillimeter-wave transitions have been observed. The accuracy of the frequency measurements in the klystron fundamental frequency region can be estimated to be of the order of ±0.001 to ±0.005 MHz, giving an improvement over our earlier microwave measurements on HCNO [1–3] by approximately a factor of 50. This was achieved primarily by employing the signal averaging technique and computer filtering simultaneously for both the absorption line and the frequency marker, but also, by providing a temperature controlled oil bath for the driver klystron, and by maximizing the lifetime of HCNO to 10 hours or more in the free space cell compared to 7 minutes in a conventional X-band Stark cell. The crystal-controlled frequency standard was monitored against the 151 kHz standard frequency of the Deutschlandfunk. The frequency comparison can be carried out to within a factor of $\pm 5 \times 10^{-11}$ employing 2000 sec observation time [6].

In addition to the absorptions due to molecules in the ground state of HCNO, vibrational satellites were measured for a large number of excited vibrational states [7] (see also Fig. 1). This note presents the absorption frequencies and the rotational constants obtained from the anlysis for the ground state, and for the first excited state of each of the two vibrational bending modes, ν_4 and ν_5. Figure 1 shows an oscilloscope trace of the $J = 5 \rightarrow 6$ transition at approximately 137.6 GHz.

The ground state lines, which are listed in Table 1, were fitted to the expression

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

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Table 1. Observed and calculated frequencies of rotational transitions in the ground state of $H\,^{12}C\,^{14}N\,^{16}O$.

$J \rightarrow J+1$	Rigid rotor frequencies MHz	Centrifugal distortion contribution MHz	Calculated frequencies[a] MHz	Observed frequencies[b] MHz	Deviations[d] MHz
$0 \rightarrow 1$	22 938.103	− 0.017	22 938.086	22 938.070[e]	− 0.016
$1 \rightarrow 2$	45 876.205	− 0.136	45 876.069	45 876.070	0.001
$2 \rightarrow 3$	68 814.308	− 0.460	68 813.848	68 813.860	0.012
$3 \rightarrow 4$	91 752.411	− 1.091	91 751.320	91 751.320	0.000
$4 \rightarrow 5$	114 690.514	− 2.131	114 688.383	114 688.382	− 0.001
$5 \rightarrow 6$	137 628.616	− 3.682	137 624.934	137 624.957	0.023
$6 \rightarrow 7$	160 566.719	− 5.847	160 560.872	160 560.862	− 0.010
$7 \rightarrow 8$	183 504.822	− 8.728	183 496.093	183 496.084	− 0.009
$8 \rightarrow 9$	206 442.925	− 12.428	206 430.497	206 430.491	− 0.006
$9 \rightarrow 10$	229 381.027	− 17.048	229 363.980	229 363.967	− 0.013
$10 \rightarrow 11$	252 319.130	− 22.691	252 296.440	252 296.454	0.015
$11 \rightarrow 12$	275 257.233	− 29.458	275 227.774	275 227.774	0.000
$14 \rightarrow 15$	344 071.541	− 57.536	344 014.005	344 013.522[c]	− 0.483
$17 \rightarrow 18$	412 885.849	− 99.422	412 786.427	412 786.066[c]	− 0.361

[a] The calculated line frequencies were obtained by using the constants in Table 5.

[b] The estimated experimentall error for all mm-wave lines is ±0.015 MHz except for the two sub-mm-wave lines listed whose estimated experimental error is ±0.50 MHz.

[c] These lines were not included in the centrifugal distortion analysis.

[d] Standard deviation of the fit is ±0.012 MHz.

[e] From. Ref. [1].

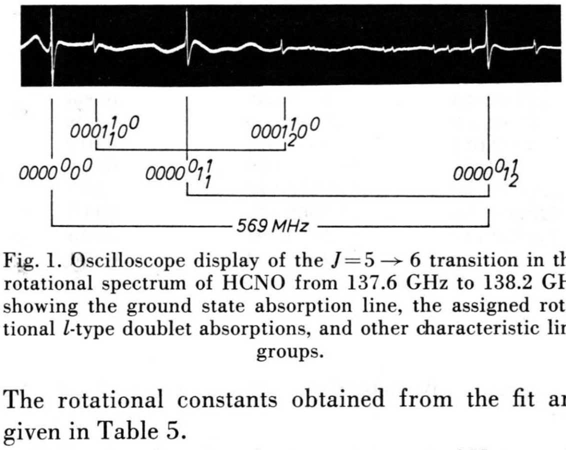

Fig. 1. Oscilloscope display of the $J=5 \rightarrow 6$ transition in the rotational spectrum of HCNO from 137.6 GHz to 138.2 GHz showing the ground state absorption line, the assigned rotational *l*-type doublet absorptions, and other characteristic line groups.

The rotational constants obtained from the fit are given in Table 5.

Following the perturbation treatment of NIELSEN[8], the energy eigenvalues of a linear molecule in a singly excited vibrational bending mode ($\nu_t = l = 1$, with $t = 4,5$) are

$$\varepsilon = E_0 \pm W$$

where E_0 is the unperturbed energy, $E_0 = E_\mathrm{v} + E_\mathrm{r}$, and

$$\begin{aligned} E_\mathrm{r} &= B_v[J(J+1) - l^2] - D_\mathrm{v}[J(J+1) - l^2]^2 \\ &= -[B_\mathrm{v} + D_\mathrm{v}] + [B_\mathrm{v} + 2\,D_\mathrm{v}]\;J(J+1) \\ &\quad - D_\mathrm{v}[J(J+1)]^2. \end{aligned}$$

The perturbation term W is given by

$$W = \tfrac{1}{2}\,\{q_t^{(0)}\,J(J+1) - q_t^{(1)}\,J^2(J+1)^2\}\,.$$

In the expression for W, allowance has been made for centrifugal distortion effects on the *l*-type doubling perturbation. According to the electric dipole selection rules, the observed rotational frequencies will be

$$\begin{aligned} \nu_\pm &= 2(J+1)\,(B_\mathrm{v} + 2\,D_\mathrm{v}) - 4(J+1)^3\,D_\mathrm{v} \\ &\quad \pm \tfrac{1}{2}\,\{2(J+1)\;q_t^{(0)} - 4(J+1)^3\,q_t^{(1)}\}\,. \end{aligned}$$

It can be seen that the unperturbed rotational constants can be obtained by carrying out a centrifugal distortion analysis of the average of the two lines occurring for each J value, $(\nu_+ + \nu_-)/2$; the correlation between B_v and D_v is negligible. Similarly, the difference between the two frequencies, $\nu_+ - \nu_-$, can be fitted in just the same way to find the value of the *l*-type doubling constants. The observed frequencies are listed in Tables 2 and 3, together with the center frequency of each doublet. The differences between each doublet are listed in Table 4, and the constants obtained following the above procedure are given in Table 5. In order to facilitate comparison with infrared data, in which bands due to individual components of *l*-type doublets are usually analyzed separately, the rotational constants obtained when the rotational frequencies

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[8] H. H. NIELSEN, Handbuch der Physik, Band XXXVII/1, Atome III — Moleküle I (Springer-Verlag, Berlin 1959), The Vibration-Rotation Energies of Molecules and their Spectra in the Infrared, Page 277, 278.

Table 2. Observed and calculated frequencies of rotational l-type doublet transitions in the 0001^10^0 vibrational state of $H\,^{12}C\,^{14}N\,^{16}O$.

$J \rightarrow J+1$	Observed doublet[a]		Center of observed doublet	Center of calculated doublet[b]	Deviations[c]
	$0001^1_10^0$ MHz	$0001^1_20^0$ MHz	MHz	MHz	MHz
1 → 2	45 886.228	45 980.911	45 933.570	45 933.573	– 0.003
2 → 3	68 829.118	68 971.127	68 900.123	68 900.118	0.005
3 → 4	91 771.742	91 961.010	91 866.376	91 866.373	0.003
4 → 5	114 714.030	114 950.447	114 832.238	114 832.242	– 0.004
5 → 6	137 655.858	137 939.397	137 797.628	137 797.628	0.000
6 → 7	160 597.142	160 927.783	160 762.463	160 762.434	0.029
7 → 8	183 537.767	183 915.337	183 726.552	183 726.565	– 0.013
8 → 9	206 477.734	206 902.107	206 689.920	206 689.923	– 0.002
9 → 10	229 416.852	229 887.932	229 652.392	229 652.411	0.019
10 → 11	252 355.115	252 872.741	252 613.928	252 613.934	– 0.006
11 → 12	275 292.387	275 856.431	275 574.409	275 547.394	0.015

[a] The estimated experimental error for all mm-wave lines is ±0.015 MHz.
[b] The calculated frequencies were obtained by using the constants in Table 5.
[c] Standard deviation of the fit is ±0.014 MHz.

Table 3. Observed and calculated frequencies of rotational l-type doublet transitions in the 0000^01^1 vibrational state in $H\,^{12}C\,^{14}N\,^{16}O$.

$J \rightarrow J+1$	Observed doublet[a]		Center of observed doublet	Center of calculated doublet[b]	Deviations[c]
	$0000^01^1_1$ MHz	00001^1_2 MHz	MHz	MHz	MHz
1 → 2	45 927.335	46 065.870	45 996.603	45 996.581	0.022
2 → 3	68 890.694	69 098.543	68 994.619	68 994.613	0.006
3 → 4	91 853.809	92 130.872	91 992.340	91 992.337	0.003
4 → 5	114 816.506	115 162.802	114 989.654	114 989.648	0.006
5 → 6	137 778.700	138 194.206	137 986.453	137 986.445	0.008
6 → 7	160 740.259	161 224.963	160 982.611	160 982.623	– 0.012
7 → 8	183 701.114	184 255.028	183 978.071	183 978.079	– 0.008
8 → 9	206 661.197	207 284.203	206 972.700	206 972.712	– 0.012
9 → 10	229 620.344	230 312.473	229 966.409	229 966.417	– 0.008
10 → 11	252 578.507	253 339.712	252 959.110	252 959.092	0.018
11 → 12	275 535.454	276 365.810	275 950.632	275 950.633	– 0.001

[a] The estimated experimental error for all mm-wave lines is ±0.015 MHz.
[b] The calculated frequencies were obtained by using the constants given in Table 5.
[c] Standard deviation of the fit is ±0.012 MHz.

Table 4. Observed and calculated splittings of the rotational l-type doublets for the 0000^01^1 and 0001^10^0 vibrational states in $H\,^{12}C\,^{14}N\,^{16}O$.

$J \rightarrow J+1$	Doublet separation for 0000^01^1		Deviations[c]	Doublet separation for 0001^10^0		Deviations[d]
	observed[a] MHz	calculated[b] MHz	MHz	observed[a] MHz	calculated[b] MHz	MHz
1 → 2	138.535	138.538	– 0.003	94.683	94.678	0.005
2 → 3	207.849	207.799	0.050	142.009	141.981	0.028
3 → 4	277.063	277.050	0.013	189.269	189.241	0.028
4 → 5	346.296	346.288	0.008	236.417	236.443	– 0.026
5 → 6	415.507	415.509	– 0.002	283.539	283.573	– 0.034
6 → 7	484.705	484.710	– 0.005	330.641	330.617	0.025
7 → 8	553.913	553.887	0.026	377.570	377.559	0.011
8 → 9	623.006	623.039	– 0.033	424.373	424.386	– 0.013
9 → 10	692.129	692.160	– 0.031	471.080	471.084	– 0.004
10 → 11	761.205	761.248	– 0.043	517.626	517.637	– 0.011
11 → 12	830.356	830.300	0.056	564.044	564.031	0.013

[a] The estimated experimental error of the separation is ±0.030 MHz.
[b] The calculated splittings were obtained using the constants given in Table 5.
[c] The standard deviation of the fit is ±0.034 MHz.
[d] The standard deviation of the fit is ±0.022 MHz.

Table 5. Molecular constants [a] of H ^{12}C ^{14}N ^{16}O obtained from the centrifugal distortion analysis.

Vibrational state					B_{v} (MHz)	D_{v} (kHz)	$q_t^{(0)}$ (MHz)	$q_t^{(1)}$ (kHz)
v_1	v_2	v_3	v_4^l	v^l				
0	0	0	0^0	0^0	11469.05137 ± 0.00061	4.2619 ± 0.0030	—	—
0	0	0	0^0	1^1	11499.17090 ± 0.00061	4.2932 ± 0.0030	34.6354 ± 0.0017	0.1384 ± 0.0083
0	0	0	1^1	0^0	11483.41734 ± 0.00066	4.0242 ± 0.0033	23.6732 ± 0.0011	0.6009 ± 0.0055

[a] All errors quoted are standard errors.

Table 6. Rotational constants of the individual components of the rotational l-type doublet transitions [a].

Vibrational state					B_{v} (MHz)	D_{v} (kHz)
v_1	v_2	v_3	v_4^l	v_5^l		
0	0	0	0^0	1_1^1	11481.85319 ± 0.00104	4.2240 ± 0.0052
0	0	0	0^0	1_2^1	11516.48860 ± 0.00103	4.3624 ± 0.0051
0	0	0	1_1^1	0^0	11471.58076 ± 0.00065	3.7238 ± 0.0032
0	0	0	1_2^1	0^0	11495.25392 ± 0.00103	4.3246 ± 0.0051

[a] All errors quoted are standard errors.

for each component are fitted separately are given in Table 6.

Although the analysis was attempted with P^6 terms included, no significant value of H_{v} or of $q_t^{(2)}$ was obtained. In contrast, the microwave measurements of the direct l-type doublet transitions did yield a significant value of $q_4^{(2)}$ and of $q_5^{(2)}$. Obviously, the maximum J value of $J = 11$ of the observed rotational transitions is not high enough to allow the independent determination of these constants. For both $\nu_4 = 1$ and $\nu_5 = 1$, the values obtained from the direct l-type doubling transitions [1] for $q_t^{(0)}$ and $q_t^{(1)}$ are within three times the standard error of the constants obtained from the present data. The former constants, from Ref. [1], are; more reliable, due to the larger number of points measured and the much higher J values attained (up to $J = 37$). However, considering the small magnitude of $q_t^{(1)}$, the agreement found is an indication of the accuracy with which information can be extracted from the millimeter-wave measurements.

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