Nuclear Quadrupole Hyperfine Structure of the Direct *l*-Type Transitions of the Fulminic Acid Isotopomers $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$

Jürgen Preusser* and Manfred Winnewisser
Physikalisch-Chemisches Institut der Justus-Liebig-Universität,
Heinrich-Buff-Ring 58, D-35392 Gießen

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The direct *l*-type transitions of $H^{13}C^{14}N^{16}O$ in the vibrational states $(v_4 v_5)$ = (01) and (03) were measured in the frequency range from 18 to 40 GHz. These transitions show a nuclear quadrupole hyperfine structure caused by the ^{14}N nucleus, which could partially be resolved at Doppler-limited resolution. The analogous transitions of the parent species, $H^{12}C^{14}N^{16}O$, were remeasured. They displayed a very similar hyperfine structure, also partially resolved. The hyperfine patterns of both $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$ were analysed by means of contour fittings to the absorption profiles. The parameter $\eta_5 eQq$, which is responsible for the splittings, is determined to be 645(20) kHz for the vibrational state (01) and 890(44) kHz for the vibrational state (03) for $H^{12}C^{14}N^{16}O$ and 642(32) kHz for (01) and 898(22) kHz for (03) for $H^{13}C^{14}N^{16}O$. This unexpectedly large splitting parameter for states involving the large amplitude motion ν_5 (HCN bending) is discussed as another consequence of the quasilinearity of fulminic acid, in view of the fact that the analogous transitions for the vibrational state (10) (NCO bending) do not split or even show a significant line broadening at the resolution used for the present measurements.

Key words: Nuclear quadrupole hyperfine structure, quasilinear molecule, microwave spectroscopy

Introduction

The direct *l*-type transitions of the parent species of fulminic acid, $H^{12}C^{14}N^{16}O$, were measured by Winnewisser and Bodenseh [1] in the vibrational state $(v_4 v_5)$ = (01) and by Bodenseh and Winnewisser [2] in the vibrational state (03) in 1967 and 1969, respectively. The quantum numbers v_1, v_2, and v_3 were zero for all vibrational states considered in those papers and were therefore omitted in the designation of the states. The measurement technique at that time did not allow the detection of a hyperfine splitting of these transitions caused by the nuclear quadrupole moment of the ^{14}N nucleus. Hüttner et al. [3] analyzed the hyperfine structure of the pure rotational transitions $J = 1 \leftarrow 0$ of $H^{12}C^{14}N^{16}O$ and $D^{12}C^{14}N^{16}O$ for the vibrational ground state. They found a ^{14}N-coupling constant of eQq = 245(5) kHz for both isotopomers, which is very small compared to the analogous constant for $H^{12}C^{14}N$ with $eQq = -4.809\,2(11)$ MHz [4] and $H^{13}C^{14}N$ with $eQq = -4.737(28)$ MHz [5]. There are no data available dealing with nuclear quadrupole hyperfine structures of pure rotational transitions and direct *l*-type transitions in excited vibrational states of $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$, as is the case for $H^{12}C^{14}N$ and $H^{13}C^{14}N$ [5, 6].

In this work the direct *l*-type transitions were measured for $H^{13}C^{14}N^{16}O$ and remeasured for $H^{12}C^{14}N^{16}O$ in the microwave region from 18 to 40 GHz in the vibrational states $(v_4 v_5)$ = (01), (03), and (10), respectively, from which only those in excited states of the quasilinear HCN-bending mode ν_5 are discussed in this paper. The transitions in the states (10) do not show any hyperfine splitting within Doppler resolution for both isotopic species. These transitions were already published in previous analyses [1, 7].

The splitting of direct *l*-type transitions in excited states of the quasilinear bending mode is dominated by the constant $\eta_5 eQq$, which is the product of the nuclear quadrupole coupling constant eQq and the asymmetry parameter η_5. The asymmetry of the nuclear quadrupole coupling tensor is induced by the ex-

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* Present address: University of British Columbia, Department of Chemisty, 2036 Main Mall, B. C. V6T 1Z1, Canada.
Reprint requests to Prof. M. Winnewisser.

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citation of the ν_5. The analogous product $\eta_2 eQq$ was determined for $H^{12}C^{14}N$ in several studies [4, 8 - 10]. The best value of this constant, $\eta_2 eQq = 392(5)$ kHz, can be found in the paper of Fliege et al. [10], because they were the first using sub-Doppler resolution. Since the absolute value of eQq for $H^{12}C^{14}N^{16}O$ is smaller than the same value for $H^{12}C^{14}N$ by a factor of approximately 20, it was assumed that $\eta_5 eQq$ for $H^{12}C^{14}N^{16}O$ should be smaller than $\eta_2 eQq$ for $H^{12}C^{14}N$ also by this factor. This would lead to a much smaller splitting of the direct l-type transitions for $H^{12}C^{14}N^{16}O$ compared to $H^{12}C^{14}N$, which would not have been resolvable even with the very high resolution of Fliege et al. [10]. For this reason, a hyperfine splitting of the direct l-type transitions of $H^{12}C^{14}N^{16}O$ in excited states of both bending motions was not expected to be resolvable at Doppler-limited resolution.

However, the direct l-type transitions of $H^{13}C^{14}N^{16}O$ in the vibrational states (01) and (03) revealed a splitting into close doublets with a relative intensity of approximately 1:2. Preliminary center frequencies of these doublets, using this relative intensity estimate as weighting factor, were already used in the determination of the l-type splitting constants q_v, q_{vJ}, and q_{vJJ} in the paper by Winnewisser et al. [7]. The present paper deals with the precise analysis of these doublets. Having observed these splittings for $H^{13}C^{14}N^{16}O$, the analogous transitions of the parent species, $H^{12}C^{14}N^{16}O$, were remeasured. They could be resolved into very similar close doublets and their analysis is also presented in this paper. The analogous transitions of the isotopomers $H^{12}C^{15}N^{16}O$ [11] and $H^{13}C^{15}N^{16}O$ [12] of course do not show any splitting, because the ^{15}N nucleus has no quadrupole moment.

Experimental Details

Both HCNO samples were produced according to the efficient synthesis published by Wentrup et al. [13] by gas-phase pyrolysis of 3-phenyl-4-oximino-isoxazol-5(4H)-one. The precursor for the $H^{13}C^{14}N^{16}O$ isotopomer was prepared by a modified synthesis according to Wilmes and Winnewisser [14], starting with isotopically enriched $^{13}CH_3COONa$ (99 % ^{13}C).

The spectra were recorded using a Stark-effect spectrometer (Hewlett-Packard 8560A Microwave Rotational Resonance Spectrometer) employing square-wave Stark-modulation at 33.3 kHz modulation frequency. For all measurements of the direct l-type transitions we used an electric field strength of 3600–4000 V/cm. A continuous-flow system with a dynamic pressure of approximately 1–2 Pa was established, since the lifetime of the HCNO sample in the metal waveguide cell was only $\tau_{1/2} < 2$ min. This continuous flow turned out to be essential for the observation of the hyperfine splitting, because this was the only practical way to achieve sample pressures low enough to observe the transitions with nearly Doppler-limited linewidth and without an observable decrease of the sample concentration during the measurement of one transition.

The spectra from the Stark-effect spectrometer, registered by a chart recorder, were digitized in order to allow a detailed analysis of the observed doublets by contour fitting. Using this fitting procedure it was possible to determine the hypothetical center frequency of each doublet with a relative precision better than 1 kHz, while their absolute errors are limited to the instrumental precision. The absolute experimental errors for all lines in this region can be estimated to range from ±10 kHz to ±20 kHz, depending on the signal-to-noise ratio. The relative errors within one observed multiplet are in all cases smaller than 1 kHz.

Theory

In the case of $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$ the most important contribution to the nuclear hyperfine splitting of the rovibrational energy levels is the coupling with the nuclear electric quadrupole moment of the ^{14}N-nucleus.

The quadrupole energy E_Q within the framework of a linear molecule given by Javan [15] and Radford and Kurtz [4] is

$$\frac{E_Q}{h} = eQq\left[\frac{3l^2 - J(J+1)}{J(J+1)} \pm \frac{\eta}{2}\right] f(I, J, F), \quad (1)$$

where $f(I, J, F)$ represents Casimir's function. The constant eQq is the nuclear electric quadrupole coupling constant in frequency units. The constant η is only used for the $|l| = 1$ levels. It describes the anisotropy of the molecular electric field gradient caused by a bending vibration of a linear molecule. Following the convention of Radford and Kurtz [4], the positive (negative) sign in (1) stands for the e(f) levels. The formula is identical to that describing a "slightly asymmetric prolate rotor" with an asymmetry parameter $b_p = 0$. With a nuclear spin quantum number $I = 1$ for the ^{14}N nucleus and $F = J + I, J + I - 1, \ldots, |J - I|$, this leads to a splitting of each rovibrational level into three sublevels with $F = J, J \pm 1$ (except for unsplit levels with $J = 0$).

In addition there are small perturbations of all energy levels due to spin-rotation interactions of H, ^{13}C and ^{14}N atoms, from which the most significant contribution is due to the nitrogen atom. All these effects are neglected here, because the resolution of the present measurements is not high enough to allow the analysis even of the strongest of these minor effects and because there are no experimental data on these interactions available for HCNO isotopomers which could have been used in the present analysis. Using the assumption of no additional spin-rotation interactions and the fact that for the direct l-type transitions considered here J' equals J'', the frequency shifts $\Delta\nu$ of the quadrupole components relative to a hypothetical center frequency of a direct l-type transition (assuming that the e level is the lower one, which is true for both species considered) are given by

$$\begin{aligned}\Delta\nu = {} & eQq\frac{3l^2 - J(J+1)}{J(J+1)} \\ & \cdot \left[f(I,J,F') - f(I,J,F'')\right] \\ & - \frac{\eta eQq}{2}\left[f(I,J,F') + f(I,J,F'')\right].\end{aligned} \qquad (2)$$

If one considers the theoretical relative intensities for the allowed hyperfine components with $\Delta F = 0, \pm 1$, only the $\Delta F = \Delta J = 0$ transitions will remain strong when J increases. In addition, the relative intensities of these strong components become more and more equal with increasing J. The formulae to calculate these relative intensities can be found in the standard text books given in [16, 17] and are not repeated here.

The lowest J value of the measured transitions presented in this paper is 18. This leads to relative intensities of the $\Delta F = \pm 1$ transitions of less than 0.4 % of the intensity of the weakest of the three $\Delta F = 0$ components and this percentage still decreases with increasing J. In the present measurements it was impossible to detect these weak $\Delta F = \pm 1$ hyperfine components. As a consequence of these intensity considerations, three components with approximately the same intensity have to be expected while the three $\Delta F = \pm 1$ components are to weak to be observed. If one concentrates on the three $\Delta F = 0$ components ($F' = F''$), (2) simplifies considerably and the transition frequency ν of each component is given by

$$\nu = \nu_c - \eta eQq\; f(I, J, F), \qquad (3)$$

where ν_c is the hypothetical center frequency of the hyperfine multiplet. Unfortunately the constants η and eQq cannot be determined at the same time using only the information from the splitting of the direct l-type transitions. In order to obtain the necessary additional information, the analysis of the hyperfine structure of the pure rotational transitions in the same vibrational states would be required. The most important transitions for getting this information are the $J = 2 \leftarrow 1$ transitions in the substates $(01)^{1e,f}$ and $(03)^{1e,f}$, but these have not yet been measured at sufficiently high resolution to analyze their hyperfine structure.

For $H^{12}C^{14}N$ and $H^{13}C^{14}N$ the v_2 dependence of eQq is significant but small. The change is approximately 2 % per added quantum of ν_2 [5, 6]. In order to estimate a value of eQq of $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$ in excited states of the HCN-bending mode one may assume a similar change of eQq with increasing vibrational quantum number v_5. However, this assumption may be wrong, since the ν_5 of fulminic acid is known to exhibit a large-amplitude motion.

Data Analysis

In order to adjust the center frequencies ν_c and the constants $\eta_5 eQq$, the analysis of the observed spectra was performed by a nonlinear least-squares contour fitting routine which has been developed under the computer algebra system Mathematica**. This fitting routine adjusts the center frequency ν_c of a multiplet, the splitting parameter $\eta_5 eQq$, the linewidth, an intensity scaling factor and a baseline offset, using the well known Levenberg-Marquardt method. A Gaussian lineshape function was assumed for each of the three strong components defined by (3) for the transitions in the vibrational states (01) for both HCNO isotopomers. This was appropriate, because the observed

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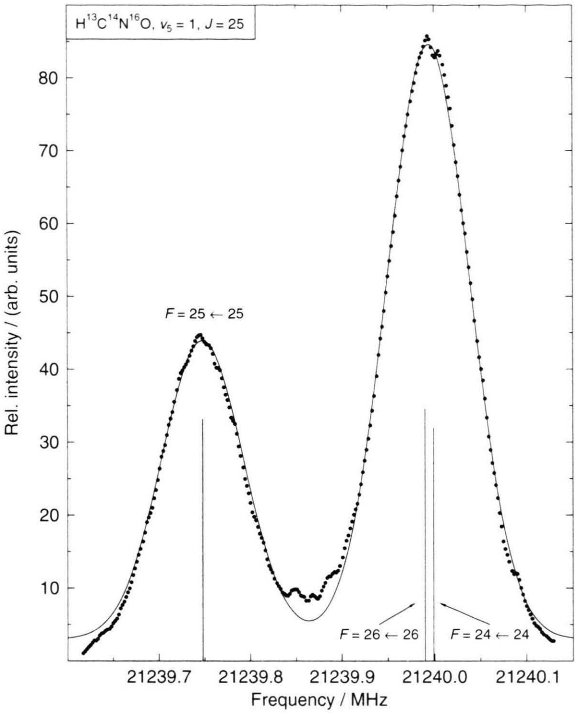

Fig. 1. Sample spectrum showing the ^{14}N nuclear quadrupole hyperfine pattern of the direct l-type transition $J = 25 \leftarrow 25$ for $H^{13}C^{14}N^{16}O$ in the vibrational state $(v_4 v_5) = (01)$. The dots are the digitized and scaled experimental data, the solid line is the fitted pattern assuming Gaussian lineshape functions.

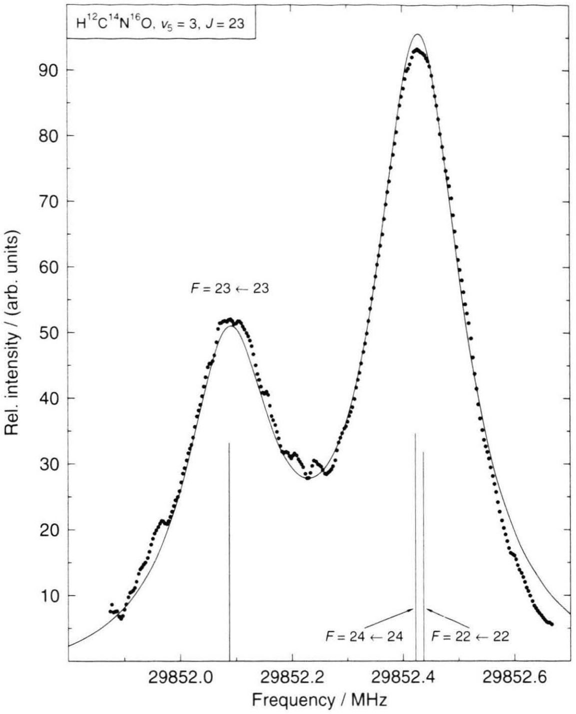

Fig. 2. Sample spectrum showing the ^{14}N nuclear quadrupole hyperfine pattern of the direct l-type transition $J = 23 \leftarrow 23$ for $H^{12}C^{14}N^{16}O$ in the vibrational state $(v_4 v_5) = (03)$. The dots are the digitized and scaled experimental data, the solid line is the fitted pattern assuming Lorentzian lineshape functions.

linewidth was only slightly larger than the expected Doppler width. In the case of the weaker transitions arising from the less populated vibrational state (03), it was necessary to use a higher sample pressure to achieve sample concentrations high enough to obtain a satisfactory signal-to-noise ratio. Since this procedure lead to considerably pressure broadened lines, we assumed a Lorentzian lineshape function for these transitions.

Figure 1 gives an example of the result of the fitting procedure for the $J = 25 \leftarrow 25$ transition of $H^{13}C^{14}N^{16}O$ in the vibrational state (01) using a Gaussian lineshape function. An example for a typical spectrum in the state (03) is given in Fig. 2, which shows the $J = 23 \leftarrow 23$ transition of $H^{12}C^{14}N^{16}O$. In this particular case a Lorentzian lineshape function was used.

Table 1. Obtained values for $\eta_5 eQq$ for $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$ in the vibrational states $(v_4 v_5) = (01)$ and (03).

State	$H^{12}C^{14}N^{16}O$	$H^{13}C^{14}N^{16}O$
(01)	645(20) kHz	642(32) kHz
(03)	890(44) kHz	898(22) kHz

Values in parentheses are the estimated errors in the last digits (twice the standard error).

In each case it was possible to calculate the unperturbed center frequency ν_c with an error of much less than 1 kHz, which is the same order of magnitude as the expected relative frequency precision of the measurements. The absolute error of the center frequency (and of the calculated frequencies for each hyperfine component), however, can be estimated to be approximately ±10 kHz for absorption lines arising in the vibrational state (01) and ±20 kHz in the vibrational state (03).

The values of $\eta_5 eQq$ obtained for all the multiplets of a given species and a given vibrational state were averaged, because a significant J dependence could not be observed within the standard deviation. The resulting values are given in Table 1. The standard

Table 2. Observed direct l-type transitions of $H^{12}C^{14}N^{16}O$ in the vibrational state $(v_4v_5) = (01)$.

$J' \leftarrow J''$	$F' \leftarrow F''$	$\nu_{obs.}$/MHz	$\nu_{calc.}$/MHz	I_{calc}	ν_{center}/MHz
23 ← 23	22 ← 22	} 19 071.515	19 071.516	0.3185	
	24 ← 24		19 071.506	0.3469	19 071.432
	23 ← 23	19 071.270	19 071.274	0.3321	
24 ← 24	23 ← 23	} 20 725.277	20 725.284	0.3192	
	25 ← 25		20 725.274	0.3464	20 725.197
	24 ← 24	20 725.029	20 725.034	0.3322	
25 ← 25	24 ← 24	} 22 447.139	22 447.140	0.3197	
	26 ← 26		22 447.130	0.3459	22 447.056
	25 ← 25	22 446.894	22 446.898	0.3323	
26 ← 26	25 ← 25	} 24 237.050	24 237.059	0.3203	
	27 ← 27		24 237.050	0.3454	24 236.973
	26 ← 26	24 236.805	24 236.811	0.3324	
27 ← 27	26 ← 26	} 26 094.870	26 094.871	0.3208	
	28 ← 28		26 094.862	0.3450	26 094.787
	27 ← 27	26 094.623	26 094.627	0.3325	
28 ← 28	27 ← 27	} 28 020.521	28 020.525	0.3212	
	29 ← 29		28 020.516	0.3446	28 020.439
	28 ← 28	28 020.274	28 020.277	0.3325	
29 ← 29	28 ← 28	} 30 013.887	30 013.884	0.3217	
	30 ← 30		30 013.875	0.3442	30 013.799
	29 ← 29	30 013.639	30 013.638	0.3326	
30 ← 30	29 ← 29	} 32 074.856	32 074.860	0.3220	
	31 ← 31		32 074.852	0.3439	32 074.775
	30 ← 30	32 074.609	32 074.614	0.3326	
31 ← 31	30 ← 30	} 34 203.322	34 203.330	0.3224	
	32 ← 32		34 203.322	0.3436	34 203.244
	31 ← 31	34 203.074	34 203.081	0.3327	
32 ← 32	31 ← 31	} 36 399.161	36 399.170	0.3228	
	33 ← 33		36 399.163	0.3433	36 399.083
	32 ← 32	36 398.913	36 398.917	0.3327	
33 ← 33	32 ← 32	} 38 662.252	38 662.243	0.3231	
	34 ← 34		38 662.236	0.3430	38 662.160
	33 ← 33	38 662.003	38 662.003	0.3327	

deviation of the averaged $\eta_5 eQq$ constants is found to be between ±10 and ±22 kHz, although this constant could be determined with errors smaller than 1 kHz for each analyzed multiplet. This may be attributed to the facts that two of the components in the line profiles are very close together and the line-shape functions used in the fitting procedure were not fully appropriate. For a significant improvement of the values for the $\eta_5 eQq$ constant it will be necessary to obtain spectra at sub-Doppler resolution (10 kHz or better) which would at least partially resolve the high and low F components (see Figs. 1 and 2).

Table 3. Observed direct l-type transitions of $H^{12}C^{14}N^{16}O$ in the vibrational state $(v_4v_5) = (03)$.

$J' \leftarrow J''$	$F' \leftarrow F''$	$\nu_{obs.}$/MHz	$\nu_{calc.}$/MHz	I_{calc}	ν_{center}/MHz
18 ← 18	17 ← 17	} 18 509.124	18 509.137	0.3143	
	19 ← 19		18 509.118	0.3504	18 509.012
	18 ← 18	18 505.797	18 508.782	0.3314	
19 ← 19	18 ← 18	} 20 562.959	20 562.963	0.3154	
	20 ← 20		20 562.946	0.3496	20 562.844
	19 ← 19	20 562.640	20 562.625	0.3316	
20 ← 20	19 ← 19	} 22 724.323	22 724.324	0.3163	
	20 ← 20		22 724.309	0.3488	22 724.209
	21 ← 21	22 724.002	22 723.996	0.3317	
21 ← 21	20 ← 20	} 24 993.090	24 993.093	0.3171	
	22 ← 22		24 993.077	0.3481	24 992.974
	21 ← 21	24 992.760	24 992.754	0.3319	
22 ← 22	21 ← 21	} 27 369.162	27 369.171	0.3179	
	23 ← 23		27 369.156	0.3475	27 369.051
	22 ← 22	27 368.832	27 368.827	0.3320	
23 ← 23	22 ← 22	} 29 852.430	29 852.437	0.3185	
	24 ← 24		29 852.423	0.3469	29 852.316
	23 ← 23	29 852.094	29 852.088	0.3321	
24 ← 24	23 ← 23	} 32 442.782	32 442.788	0.3192	
	25 ← 25		32 442.774	0.3464	32 442.667
	24 ← 24	32 442.446	32 442.440	0.3322	
25 ← 25	24 ← 24	} 35 140.093	35 140.093	0.3197	
	26 ← 26		35 140.080	0.3459	35 139.979
	25 ← 25	35 139.755	35 139.763	0.3323	
26 ← 26	25 ← 25	} 37 944.247	37 944.250	0.3203	
	27 ← 27		37 944.237	0.3454	37 944.131
	26 ← 26	37 943.913	37 943.905	0.3324	

All measured and calculated transition frequencies for both species of HCNO in the vibrational states (01) and (03) are listed in Tables 2 - 5. These tables also present the relative intensities of the three observable nuclear quadrupole components, calculated and used as fixed values in the contour fitting procedure.

Discussion

The use of a continuous flow system, which enabled us to observe the lines nearly at Doppler linewidth, may be one reason why the hyperfine structure of the transitions of $H^{12}C^{14}N^{16}O$ could be observed in the present work, but could not be detected in the older work [1, 2]. Winnewisser and Bodenseh had not enough sample for a continuous-flow system because the synthesis according to Wentrup et al. [13], which enabled us to produce HCNO samples with very high

Table 4. Observed direct l-type transitions of $H^{13}C^{14}N^{16}O$ in the vibrational state $(v_4v_5) = (01)$.

$J' \leftarrow J''$	$F' \leftarrow F''$	$\nu_{obs.}$/MHz	$\nu_{calc.}$/MHz	I_{calc}	ν_{center}/MHz
23 ← 23	22 ← 22	18 045.222	18 045.228	0.3185	
	24 ← 24		18 045.218	0.3469	18 045.141
	23 ← 23	18 044.974	18 044.979	0.3321	
24 ← 24	23 ← 23	19 610.354	19 610.365	0.3192	
	25 ← 25		19 610.355	0.3464	19 610.277
	24 ← 24	19 610.105	19 610.111	0.3322	
25 ← 25	24 ← 24	21 239.995	21 239.999	0.3197	
	26 ← 26		21 239.990	0.3459	21 239.912
	25 ← 25	21 239.746	21 239.748	0.3323	
26 ← 26	25 ← 25	22 934.096	22 934.101	0.3203	
	27 ← 27		22 934.091	0.3454	22 934.013
	26 ← 26	22 933.846	22 933.848	0.3324	
27 ← 27	26 ← 26	24 692.558	24 692.560	0.3208	
	28 ← 28		24 692.551	0.3450	24 692.473
	27 ← 27	24 692.310	24 692.310	0.3325	
28 ← 28	27 ← 27	26 515.290	26 515.291	0.3212	
	29 ← 29		26 515.282	0.3446	26 515.208
	28 ← 28	26 515.047	26 515.050	0.3325	
29 ← 29	28 ← 28	28 402.207	28 402.210	0.3217	
	30 ← 30		28 402.202	0.3442	28 402.127
	29 ← 29	28 401.965	28 401.969	0.3326	
30 ← 30	29 ← 29	30 353.205	30 353.203	0.3220	
	31 ← 31		30 353.195	0.3439	30 353.122
	30 ← 30	30 352.963	30 352.969	0.3326	
31 ← 31	30 ← 30	32 368.190	32 368.188	0.3224	
	32 ← 32		32 368.180	0.3436	32 368.102
	31 ← 31	32 367.940	32 367.939	0.3327	
32 ← 32	31 ← 31	34 447.058	34 447.058	0.3228	
	33 ← 33		34 447.051	0.3433	34 446.976
	32 ← 32	34 446.816	34 446.819	0.3327	
33 ← 33	32 ← 32	36 589.704	36 589.704	0.3231	
	34 ← 34		36 589.697	0.3430	36 589.621
	33 ← 33	36 589.461	36 589.463	0.3327	
34 ← 34	33 ← 33	38 796.017	38 796.015	0.3234	
	35 ← 35		38 796.009	0.3427	38 795.934
	34 ← 34	38 795.777	38 795.778	0.3328	

Table 5. Observed direct l-type transitions of $H^{13}C^{14}N^{16}O$ in the vibrational state $(v_4v_5) = (03)$.

$J' \leftarrow J''$	$F' \leftarrow F''$	$\nu_{obs.}$/MHz	$\nu_{calc.}$/MHz	I_{calc}	ν_{center}/MHz
19 ← 19	18 ← 18	19 450.356	19 450.364	0.3154	
	20 ← 20		19 450.346	0.3496	19 450.242
	19 ← 19	19 450.030	19 450.016	0.3316	
20 ← 20	19 ← 19	21 494.969	21 494.989	0.3163	
	21 ← 21		21 494.972	0.3488	21 494.868
	20 ← 20	21 494.642	21 494.645	0.3317	
21 ← 21	20 ← 20	23 641.207	23 641.213	0.3171	
	22 ← 22		23 641.197	0.3481	23 641.091
	21 ← 21	23 640.876	23 640.864	0.3319	
22 ← 22	21 ← 21	25 889.000	25 889.007	0.3179	
	23 ← 23		25 888.992	0.3475	25 888.890
	22 ← 22	25 888.695	25 888.672	0.3320	
23 ← 23	22 ← 22	28 238.268	—[a]	0.3185	
	24 ← 24		—	0.3469	28 238.157
	23 ← 23	28 237.935	—	0.3321	
24 ← 24	23 ← 23	30 688.889	—	0.3192	
	25 ← 25		—	0.3464	30 688.778
	24 ← 24	30 688.556	—	0.3322	
25 ← 25	24 ← 24	33 240.765	33 240.768	0.3197	
	26 ← 26		33 240.755	0.3459	33 240.648
	25 ← 25	33 240.434	33 240.420	0.3323	
26 ← 26	25 ← 25	35 893.791	35 893.791	0.3203	
	27 ← 27		35 893.778	0.3454	35 893.672
	26 ← 26	35 893.459	35 893.448	0.3324	
27 ← 27	26 ← 26	38 647.838	38 647.843	0.3208	
	28 ← 28		38 647.831	0.3450	38 647.725
	27 ← 27	38 647.507	38 647.500	0.3325	

[a] Hyperfine structure could not be fitted because of poor signal-to-noise ratio. The center frequencies are estimated by an 2:1 intensity-weighted average.

yield, was not yet known at that time. A second point may be that Winnewisser and Bodenseh used a sinewave Stark-modulation at 100 kHz [18], which causes an additional modulation broadening which may have hidden the nuclear quadrupole hyperfine structure. A third, and maybe the most important point, could be that they did not observe a splitting because at that time it was not expected and was therefore not sought.

The unexpectedly large value of the constant $\eta_5 eQq$ for fulminic acid isotopomers containing ^{14}N may be interpreted as a consequence of the quasilinear structure of this molecule. The fact that there is no splitting of the direct l-type transitions in the excited states of the well-behaved CNO-bending mode ν_4 shows that $\eta_4 eQq$ is so small that the resulting splitting is smaller than the Doppler linewidth of the transition.

In order to determine the constant η_5, the constants eQq have to be determined. This has not yet been done, since eQq for the ground state is so small that it could only be determined from the pure rotational transition $J = 1 \leftarrow 0$ (which shows the largest splitting) at Doppler resolution. Since $J = 2 \leftarrow 1$ is the lowest existing transition in the excited bending states considered here, sub-Doppler measurements of at least this transition will be necessary. An even higher resolution will be necessary to resolve the analogous hyperfine structure of the direct l-type transitions in excited vibrational states of ν_4 in order to determine $\eta_4 eQq$.

If one assumes that eQq of $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$ changes only slightly with increasing v_5, which is true for $H^{12}C^{14}N$ and $H^{13}C^{14}N$ with increasing v_2 [5, 6], η_5 will have a value of approximately 2.5 for both species. This is extremely large compared to the value of $\eta_2 = 0.08155$ for $H^{12}C^{14}N$ [10]. However, the sign of η is positive (in the framework of the convention that the positive sign in (1) belongs to the e levels) for both HCNO and HCN, which is consistent with the idea that the change in the symmetry of the electric field gradient at the ^{14}N nucleus has the same quality but an extremely different magnitude upon excitation of the HCN-bending mode in the two molecules. Since the absolute value of η_5 describes the asymmetry of the gradient of the electric field at the ^{14}N nucleus, a large value indicates a large asymmetry. In other words, HCNO behaves "more bent" than HCN, which is consistent with other spectral data. Excitation of ν_5 changes the electronic structure in the environment of the ^{14}N nucleus. This change must be much greater for HCNO than for HCN, since the HCN-bending of HCNO is known to be a large-amplitude motion. This may be explained in terms of the simple atomic orbital picture by a significant change of the hybridisation of the atomic orbitals of the carbon atom from more or less sp to sp^2, which clearly breaks the axial symmetry of the electronic field around the nitrogen atom. This change manifests itself in the magnitude of the η_5 constant.

The assumption that eQq of HCNO varies only slightly with increasing v_5 can not be proved from the present data, but there is no hint in the literature that the pure rotational transition $J = 2 \leftarrow 1$ in the vibrational state (01) shows a hyperfine splitting considerably larger than that of the vibrational ground state. However, the relative change of eQq with v_5 for $H^{12}C^{14}N^{16}O$ and $H^{13}C^{14}N^{16}O$ may be much larger than for $H^{12}C^{14}N$ and $H^{13}C^{14}N$.

The center frequencies can be used in order to obtain the l-type doubling constants q_v, q_{vJ}, and q_{vJJ} as parameters of an effective Hamiltonian for linear molecules defined by Yamada et al. [19]. In the case of $H^{13}C^{14}N^{16}O$ this was already done using weighted center frequencies for the observed doublets [7, 20]. The center frequencies obtained by the contour fits in this work do not differ from these preliminary values within the estimated absolute frequency errors of the measurements. Therefore the reanalysis did not change the values of the l-type doubling constants given in [7, 20]. For the parent species, the situation is quite similar. Previous papers dealing with the analysis of $H^{12}C^{14}N^{16}O$ data related to the l-type doubling [21 - 25] used the unresolved measurements of [1, 2]. The center frequencies obtained in this paper do not really differ from the frequencies given there, but are more precise. A new analysis combining recent high resolution FT-IR spectra and rotational spectra of $H^{12}C^{14}N^{16}O$ is in progress [26] and will use the center frequencies given in this paper. The higher precision of the center frequencies of the direct l-type transitions from this work, together with new and more precise IR data should reduce the errors for the l-type doubling constants for the parent species.

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