Laboratory Studies of the HNCO Molecular Spectrum for Precise Spectroscopy of Dark Clouds

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Abstract—Detailed studies of the internal motions of dark clouds using spectral lines of many molecules require a laboratory frequency accuracy of the order of a few m s^{-1}. Based on our laboratory studies of the HNCO rotational spectrum in the ground vibrational state, we have increased significantly the accuracy of frequency calculation in a wide range of quantum numbers. We have achieved an (1σ) uncertainty for rotational transitions in the $K_a = 0, 1$ states recalculated to the Doppler velocity scale ≤ 2 m s^{-1} for all frequencies <1.1 THz. This value allows radio-astronomical measurements with an accuracy comparable to that of the highest-precision observations based on spectral lines of other molecules.

INTRODUCTION

Detailed studies of the internal kinematics of dark clouds associated with regions of low-mass star formation require measurements of various transitions of the same molecules and spectral lines of various molecules with a very high radial-velocity accuracy. Generally, the typical width of molecular lines in dark clouds is comparable to purely thermal broadening at the characteristic kinetic temperature $T_k = 10$ K and is ~100−200 m s^{-1}. Quite often the microturbulent motions and systematic velocities attributable to collapse and rotation can also make an additional contribution. To extract correctly information about radial gas motions from Doppler line shifts or asymmetry, the laboratory frequency accuracy must be considerably higher than the magnitude of the effect being measured. Unfortunately, the overwhelming majority of the transition frequencies measured to date have experimental errors comparable to the typical widths of the spectral lines themselves in dark clouds. Thus, for example, the characteristic measurement error for many lines from the latest revision of the catalog of recommended rest frequencies for interstellar molecules (Lovas 2004) is 30−100 kHz, which corresponds to 90−300 m s^{-1} at a frequency of 100 GHz. Such an accuracy is quite sufficient for the identification and, possibly, joint analysis of various lines in

regions of massive star formation (see, e.g., Lapinov et al. 1998) with widths of several km s^{-1}, but it is unacceptable for studying the internal dynamics of dark clouds using spectral lines of various molecules.

In previous studies based on Lamb-dip measurements of nonlinear absorption in gases, we have already determined the laboratory frequencies for a number of astrophysically important molecules with an equivalent Doppler uncertainty of ≤ 1 m s^{-1}, more specifically, for C^{18}O (Cazzoli et al. 2003), ^{13}CO (Cazzoli et al. 2004), and OCS (Golubiatnikov et al. 2005). In addition, in the first paper, the currently available radio-astronomical measurements were also shown to be capable of reproducing the repeatability of the centers of the same lines from year to year with an accuracy of ≤ 1 m s^{-1}, although outliers whose causes require further studies are also possible.

This paper is devoted to laboratory studies of the rotational spectrum for an HNCO molecule in the ground vibrational state. Despite the fact that we used the method of recording the absorption profile in a gas cell based on the principle of radio-acoustic detection (RAD) (see, e.g., Golubiatnikov and Krupnov 2003) rather than the method of sub-Doppler spectroscopy in our measurements, we were able to improve significantly the description of the spectrum compared to previous measurements of other authors

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and to achieve a (1σ) prediction accuracy recalculated to the Doppler velocity scale of $\sim 0.5-2$ m s^{-1} for all frequencies <1.1 THz in $K_a = 0, 1$ owing to an upgrade of the facility and a large number of measured transitions. It is worth noting that although our interest in precision measurements stemmed from a large amount of observational data in dark clouds that were investigated simultaneously in spectral lines of many molecules, the large dipole moment of HNCO for b-type transitions between K_a ladders (Hocking et al. 1974) makes this molecules particularly attractive for investigating the radiative excitation by dust radiation in the hot cores of molecular clouds in our Galaxy (Churchwell et al. 1986; Zinchenko et al. 2000) and other galaxies (Wang et al. 2004).

DESCRIPTION OF THE SPECTRUM AND DATA ANALYSIS

Since HNCO is a slightly asymmetric prolate top with a Ray asymmetry parameter, $(2B-A-C) \times (A-C) = -0.99965$, very close to -1 (the limiting case of a symmetric prolate top), the asymptotic quantum number K_a, i.e., the angular momentum component along the molecular axis, together with the total angular momentum J, is a fairly good quantum number. The slight deviation of HNCO from a linear molecule is produced mainly by the H atom located at an angle of $123°9$ to the CN bond and a weak NCO bend of $172°6$ (Yamada 1980). As the molecule is nearly a symmetric top, for the convenience of describing the energy-level diagram, Green (1986) omitted the quantum number K_c and introduced only the additional sign $\pm K_a$ to distinguish the small energy splitting when calculating the collision rates. In this case, the negative sign always corresponds to the lower-energy levels from the K_a doublet.

The angular momentum $I = 1$ of the nitrogen nucleus with a quadrupole moment leads to an additional hyperfine splitting of rotational levels into three sublevels. This splitting becomes significant when analyzing the low-lying a-type rotational transitions in each of the K_a ladders as well as for the b-type transitions. Since the molecule is nearly a symmetric top, the splitting in HNCO can be described with a high accuracy by

$$\Delta E_Q^{\text{hf}} = eQq_{JK}Y(F,I,J), \qquad (1)$$

where

$$eQq_{JK} = \frac{J}{2J+3}\left\{\chi_{aa}\left[\frac{3K^2}{J(J+1)} - 1\right] \\ \pm \delta_{K,1}\frac{\chi_{bb} - \chi_{cc}}{2}\right\}, \qquad (2)$$

$Y(F,I,J)$ is the Casimir function,

$$Y(F,I,J) = \frac{3/4C(F,I,J)[C(F,I,J)+1] - I(I+1)J(J+1)}{2I(2I-1)J(2J-1)} \qquad (3)$$

and $C(F,I,J) = F(F+1) - I(I+1) - J(J+1)$. In Eq. (2), the positive sign corresponds to the upper energy level for the $K_a = 1$ doublet. The most accurate value of the quadrupole splitting tensor component, $\chi_{aa} = 2.0527(10)$ MHz, was obtained by Kukolich et al. (1971) in beam measurements of the $J = 1 - 0$ transition, which also revealed the smallness of the spin–rotational constant, $C_N = 0.5(2)$ kHz. The remaining components, $\chi_{bb} = -0.473(7)$ MHz and $\chi_{cc} = -1.583(7)$ MHz, were determined by Hocking et al. (1975) in a work that was the first most detailed investigation of the rotational HNCO spectrum at frequencies ≤ 210 GHz (see also Winnewisser et al. 1976) and that served as a basis for the JPL catalog accessible on the Internet at http://spec.jpl.nasa.gov (see, e.g., Pickett et al. 1998). The typical experimental accuracy achieved by Hocking et al. (1975) was $30-150$ kHz. Unfortunately, confusion in the designation of quantum numbers between the upper and lower hyperfine levels in Hocking et al. (1975) for $J = 2 - 1$ and $K_a = -1$, the error in the sign of hyperfine splittings for the individual components in $K_a = +1$, and the misprint in the b-type transition frequency at 85 GHz led to additional errors in the predictions for a number of hyperfine components from the JPL catalog. However, the data processing itself was performed by Hocking et al. (1975) correctly and the errors probably crept in only at the stage of publication and subsequent processing in the JPL catalog.

Subsequent far-infrared Fourier measurements of many spectral lines with typical experimental errors of ~ 7.5 MHz (Fusina et al. 1984) and ~ 3 MHz (Niedenhoff et al. 1995) have extended significantly the range of quantum numbers covering the measured frequencies. In addition, a few lines near 600 GHz were measured by Niedenhoff et al. (1995)

using a submillimeter spectrometer with an accuracy of ~20 kHz, which also led to an improvement in the description of the spectrum. These studies revealed a strong perturbation of the rotational HNCO spectrum due to the interaction between the ground and lower vibrational states, which is particularly strong for $K_a = 7$. They showed that the standard description of the spectrum for an asymmetric top in terms of the reduced Watson Hamiltonian (Watson 1977) is less satisfactory than that for the individual sets of effective spectroscopic constants for a linear molecule in each of the K_a states.

Despite considerable interest in describing the HNCO spectrum, the accuracy of the transition frequencies of greatest interest in studies of interstellar clouds was improved by Niedenhoff et al. (1995) only slightly. In addition, neither the JPL catalog nor the works by Hocking et al. (1975) and Niedenhoff et al. (1995) included the most accurate data obtained by Kukolich et al. (1971) for $J = 1 - 0$ in their frequency analysis. For this reason and owing to a significant improvement in the experimental accuracy of the RAD spectrometer at our disposal (see, e.g., Golubiatnikov and Krupnov 2003), which allows measurements to be made over a wide pressure range, we performed further studies of the HNCO spectrum in the frequency range 80−1100 GHz. Since we failed to resolve the hyperfine structure due to the combined Doppler broadening and pressure broadening of spectral lines, all of the corresponding line frequencies were recalculated, where necessary, to the nonsplitted transition centers using Eqs. (1) and (2). A full list of a- and b-type rotational transition frequencies measured by microwave methods and corrected for the hyperfine splitting is given in Tables 1−3.[1] In addition, in our analysis we used all of the IR data (Fusina et al. 1984; Niedenhoff et al. 1995) for which there were no submillimeter measurements with a better accuracy and on condition that these data did not fall outside the scope of the model by more than three experimental errors.

Owing to the possibility of studying the shifts of the line centers and their pressure broadening with the RAD spectrometer, we measured these parameters for a large number of transitions in the pressure range 30−500 mTorr. Within the experimental error limits, we found no line shift by pressure for the a-type transitions. At the same time, we found a fairly large shift of all b-type transitions ($\sim$ several MHz Torr^{-1}), which qualitatively appears as an energy shift of the entire ladder of levels with $K_a = 0$ almost as a whole

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[1]Tables 1−3 and 6 are published in electronic form only and are accessible via ftp cdsarc.u-strasbg.fr/pub/cats/J (130.79.128.5) or http://cdsweb.u-strasbg.fr/pub/cats/J.

downward relative to $K_a = \pm 1$. Since there are b-type transitions in the HNCO spectrum from the top downward both from $K_a = \pm 1$ to $K_a = 0$ and from $K_a = 0$ to $K_a = -1$ (see Table 2), the frequency increased with pressure for the first group and decreased for the second group. Since the isocyanic acid we studied is an unstable molecule with a lifetime of the order of several hours in the gas phase at room temperature, its sample was produced by the pyrolysis of $C_3H_3N_3O_3$, the cyanuric acid, (decomposition temperature 320°C). As HNCO was not the only decomposition product, the line shift we detected was a collective effect of all pyrolysis products. All the b-type transition frequencies from Table 2 that we measured were recalculated to the pressure-nonshifted values. All the transitions from Hocking et al. (1975) were measured at pressures <10 mTorr, when the corrections for the shift of the line centers lay within the experimental errors. At the same time, since Fusina et al. (1984) and Niedenhoff et al. (1995) performed their measurements at pressures ~1 and ~0.2 Torr, respectively, their frequencies for the b-type transitions between $K_a = \pm 1$ and 0 were not included in our model.

To analyze the absolute accuracy of the RAD spectrometer, we performed additional measurements of rotational CO transitions. When compared with the sub-Doppler measurements by Winnewisser et al. (1997), these showed agreement $\lesssim 1$ kHz for frequencies <500 GHz and ~10 kHz near 1 THz (see also Golubiatnikov and Krupnov 2003; Golubiatnikov et al. 2005).

The improvement in describing the rotational HNCO spectrum that we achieved is clearly shown in Fig. 1 for $K_a = 0$, where the results of approximating all the available frequencies for all the known rotational transitions of the ground vibrational state of HNCO by the set of effective spectroscopic constants corresponding to different K_a states were taken as a basis for the comparison. The corresponding constants used in this approach, along with a similar set from Niedenhoff et al. (1995), are given in Table 4. The solid lines symmetrically displaced relative to the zero frequency detuning (along the vertical axis) indicate the (1σ) rms statistical error in the model prediction of frequencies as a function of the total upper-level angular momentum J_{up} (lower horizontal axis) or the corresponding transition frequency (upper axis). Dash−dotted line *2* indicates the deviation relative to the basic model of the frequencies calculated in another standard approach to describing the spectrum of an asymmetric top (in the S reduction of the I^r representation of the Watson Hamiltonian; see Watson 1977; Niedenhoff et al. 1995). We see from this figure that the discrepancy between our calculations in terms of the two models is $\leq 1\sigma$ over
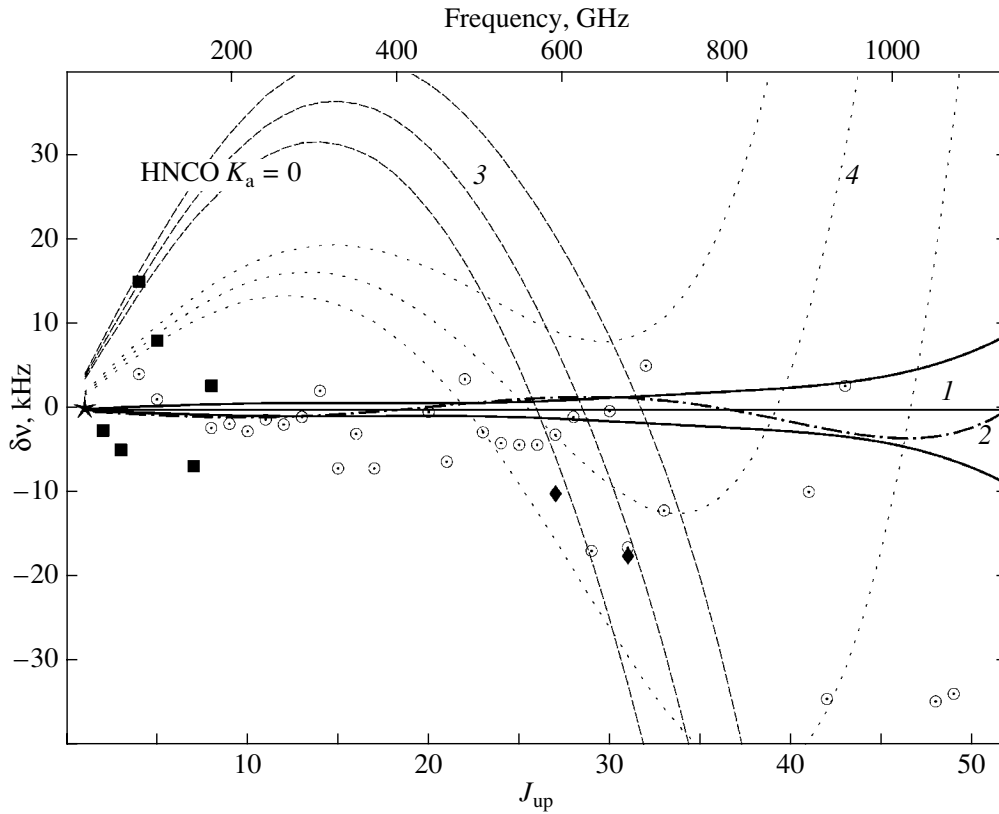
Fig. 1. Discrepancies in the predictions of HNCO rotational transition frequencies for $K_a = 0$ using different models as a function of upper-level quantum number J (lower horizontal axis) or transition frequency (upper axis). Lines *1* and *2* were constructed from our data; lines *3* and *4* were constructed using the constants from Niedenhoff et al. (1995). Our approximation by the set of constants from Table 4 was taken as the basis. Each triple of lines corresponds to the central frequency and a $\pm 1\sigma$ uncertainty. The circles, squares, diamonds, and asterisk represent, respectively, our measurements relative to the prediction of the basic model, the measurements by Hocking et al. (1975), the measurements by Niedenhoff et al. (1995), and the data by Kukolich et al. (1971).

the entire range of our measurements. We used the SPFIT computer code from Pickett's JPL software package (see, e.g., Pickett et al. 1998) to calculate the frequencies in the second approach. Since an accurate description of the frequencies of the ground vibrational state for $K_a > 5$ requires a joint analysis with the frequencies of the lower vibrational state due to the interaction between closely spaced energy levels (see Niedenhoff et al. 1995; Niedenhoff et al. 1996), which we did not measure, all the transitions from $K_a > 5$ in this approach were disregarded. The corresponding constants that we obtained in the model under consideration, along with similar estimates of other authors, are given in Table 5. With the available agreement between the estimates of different authors, Tables 4 and 5 show a significant improvement in the constants we obtained. It is worth noting that the value of the constant A from Table 5 responsible for the separation between the K_a ladders is higher than the corresponding estimate

from the JPL catalog and from Hocking et al. (1975) approximately by 6 GHz.

However, the large discrepancy in the constants B and C (accordingly in B_{eff} for $K_a = 0$ from Table 4) with respect to the quoted errors of these constants between our and previous results of Niedenhoff et al. (1995) is much more important for precision HNCO measurements in dark clouds. This discrepancy, which leads to the grossly overestimated previous rotational frequencies in $K_a = 0$ below 500 GHz, is clearly shown in Fig. 1 by curves *3* (the B, D, and H approximation by Niedenhoff et al. 1995) and *4* (the Watson approach). The main causes of this discrepancy are, first, an insufficiently high accuracy of the measurements by Hocking et al. (1975), particularly near 200 GHz, the neglect of the data by Kukolich et al. (1971), and a severely limited set of measured frequencies compared to our data. There are also similar discrepancies for other K_a ladders. This discrepancy looks particularly dramatically when recalculated to the Doppler shifts (see Fig. 2). It clearly shows that if we used the frequency predicted

Table 4. Effective spectroscopic constants of HNCO for various K_a of the ground vibrational state in the linear-top approximation (the rms uncertainties of the parameters in units of the last significant digits are given in parentheses)

K_a		Niedenhoff et al. (1995)	This paper	K_a		Niedenhoff et al. (1995)	This paper
0	B_{eff}, MHz	10990.79706(16)	10990.795120(45)	±4	B_{eff}, MHz	10978.04536(27)	10978.04552(42)
	D_{eff}, kHz	4.40870(12)	4.406883(55)		D_{eff}, kHz	3.45694(20)	3.45824(28)
	H_{eff}, mHz	3.565(32)	2.860(21)		H_{eff}, mHz	−0.667(47)	0.128(52)
	L_{eff}, μHz	−	0.1790(28)		E_0, GHz	13559.65041(72)	13559.64851(33)
−1	B_{eff}, MHz	10949.78330(13)	10949.782933(41)	±5	B_{eff}, MHz	10970.31239(22)	10970.31404(55)
	D_{eff}, kHz	3.66267(11)	3.662752(46)		D_{eff}, kHz	3.47011(12)	3.47240(38)
	H_{eff}, mHz	1.654(30)	1.951(12)		H_{eff}, mHz	−	0.996(68)
	E_0, GHz	901.722108(72)	901.721663(8)		E_0, GHz	20662.22855(84)	20662.22570(41)
+1	B_{eff}, MHz	11029.99998(12)	11029.999346(39)	±6	B_{eff}, MHz	10957.3173(15)	10957.28838(48)
	D_{eff}, kHz	3.809201(75)	3.808865(44)		D_{eff}, kHz	3.31250(43)	3.29281(51)
	H_{eff}, mHz	−	0.175(12)		H_{eff}, mHz	−	−2.97(11)
	E_0, GHz	901.722069(75)	901.721663(8)		E_0, GHz	29014.8008(13)	29014.80566(48)
−2	B_{eff}, MHz	10987.41821(17)	10987.41979(35)	±7	B_{eff}, MHz	10884.923(15)	10884.472(11)
	D_{eff}, kHz	3.638091(94)	3.64000(25)		D_{eff}, kHz	−9.826(26)	−11.169(36)
	H_{eff}, mHz	−	0.803(45)		H_{eff}, Hz	−2.695(17)	−4.370(58)
	E_0, GHz	3548.13719(45)	3548.13571(18)		L_{eff}, mHz	0.2986(34)	1.272(46)
					P_{eff}, μHz	−	−0.257(18)
+2	B_{eff}, MHz	10987.41684(22)	10987.41753(48)		S_{eff}, nHz	−	0.0244(25)
	D_{eff}, kHz	2.79263(17)	2.79496(41)		E_0, GHz	38530.8079(28)	38530.8481(14)
	H_{eff}, mHz	−2.817(35)	−1.15(14)				
	L_{eff}, μHz	−	−0.202(15)	±8	B_{eff}, MHz	10983.557(31)	10983.616(40)
	E_0, GHz	3548.13632(45)	3548.13571(18)		D_{eff}, kHz	4.708(31)	4.909(93)
					H_{eff}, Hz	−	0.185(63)
−3	B_{eff}, MHz	10983.51983(39)	10983.52076(63)		E_0, GHz	49125.5127(63)	49125.5028(49)
	D_{eff}, kHz	3.40579(34)	3.40908(44)				
	H_{eff}, mHz	−1.858(70)	−0.669(75)				
	E_0, GHz	7813.32544(63)	7813.32423(25)		χ^2	−	0.757
+3	B_{eff}, MHz	10983.51962(42)	10983.51758(64)		N_{Dat}	−	2062
	D_{eff}, kHz	3.40885(36)	3.40601(44)				
	H_{eff}, mHz	1.156(70)	0.997(74)				
	E_0, GHz	7813.32574(63)	7813.32423(25)				

Table 5. Spectroscopic constants of the ground vibrational state of HNCO in the S reduction of the I^r representation of the Watson Hamiltonian (the rms uncertainties of the parameters in units of the last significant digits are given in parentheses)

Parameter	Yamada (1980)	Fusina et al. (1984)	Niedenhoff et al. (1995)	This paper
A, GHz	918.5044(154)	918.415848(1565)	918.49365(11)	918.417805(35)
B, MHz	11071.00825(61)	11071.009010(893)	11071.01048(14)	11071.009625(56)
C, MHz	10910.57553(61)	10910.576007(841)	10910.57803(15)	10910.576840(61)
D_J, kHz	3.4863(29)	3.49350(121)	3.50114(13)	3.499956(69)
D_{JK}, kHz	931.70(65)	937.253(600)	934.858(59)	934.434(34)
D_K, MHz	6065.6(191)	5936.08(203)	6052.18(12)	5940.489(41)
d_1, Hz	$-72.995(83)$	$-73.336(228)$	$-72.828(19)$	$-73.040(22)$
d_2, Hz	$-36.5(30)$	$-31.060(422)$	$-30.542(19)$	$-30.955(37)$
H_J, mHz	—	—	0.730(51)	0.322(41)
H_{JK}, Hz	$-2.49(16)$	$-1.323(129)$	$-2.997(23)$	$-3.289(36)$
H_{KJ}, kHz	32.29(30)	34.866(312)	33.931(24)	33.698(16)
H_K, MHz	287.6(41)	242.344(555)	285.287(26)	243.8787(74)
h_1, mHz	—	0.4807(676)	—	0.0868(45)
h_2, mHz	—	—	—	0.204(11)
h_3, mHz	—	—	—	0.1467(52)
L_J, nHz	—	—	—	0.0179(79)
L_{JJK}, mHz	—	—	—	0.063(12)
L_{JK}, Hz	—	—	$0.1601(26)^*$	0.2647(49)
L_{KKJ}, kHz	$-3.163(44)^*$	$-3.5393(523)$	$-3.4074(44)^*$	$-3.3804(27)$
L_K, MHz	$-14.88(36)^*$	$-8.7679(403)$	$-14.7013(24)^*$	$-8.88309(45)$
P_{JJJK}, μHz	—	—	—	$-0.0052(14)$
P_{JJK}, μHz	—	—	—	$-7.06(86)$
P_{KKJ}, mHz	—	—	$-1.869(75)$	$-10.36(32)$
P_{KKKJ}, Hz	144.4(15)	165.40(317)	158.03(28)	156.89(17)
P_K, kHz	493.(15)	135.663(854)	486.17(10)	138.1076(89)
$S_{6,6}$, μHz	—	—	—	0.310(28)
$S_{4,8}$, mHz	—	—	—	0.1060(75)
$S_{2,10}$, Hz	$-2.494(48)^*$	$-2.8821(617)$	$-2.7453(58)^*$	$-2.7286(33)$
S_K, kHz	$-8.56(30)^*$	—	$-8.4257(20)^*$	—
T_K, Hz	58.6(22)	—	57.621(15)	—
N_{Dat}	—	946	—	1739

* For agreement with Pickett's designations, these coefficients have the opposite sign with respect to those given in the corresponding references. $S_{6,6}$, $S_{4,8}$, and $S_{2,10}$ without any letter analogue in Pickett's name file spins.nam are the coefficients of the Hamiltonian operators $\hat{J}^6\hat{J}_z^6$, $\hat{J}^4\hat{J}_z^8$, and $\hat{J}^2\hat{J}_z^{10}$; all of the remaining letter designations correspond to Pickett's ones.
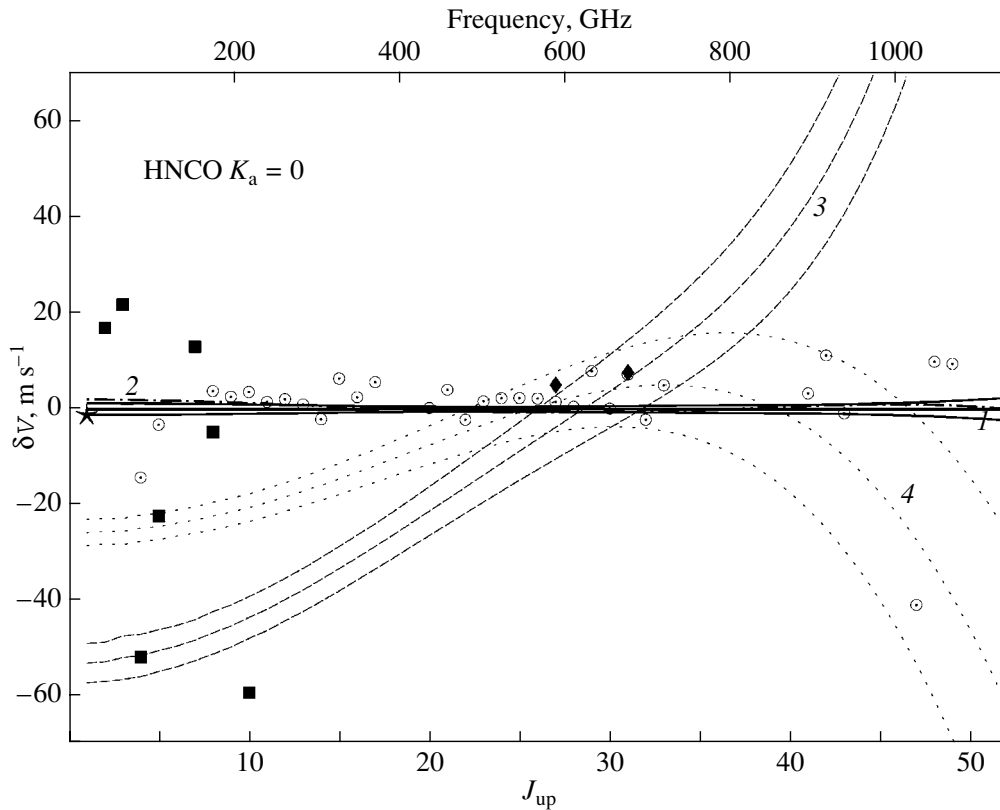
Fig. 2. Same as Fig. 1 recalculated to the Doppler shifts.

for $J = 5-4$, $K_a = 0$ based on the constants B, D, and H from Niedenhoff et al. (1995), then the systematic error would be 50 m s^{-1}, i.e., half the HNCO line FWHM at $T_k = 10$ K. In addition, it is unclear why the difference between the predictions based on the two different approaches from Niedenhoff et al. (1995) is so large.

Since the presence of a hydrogen atom, which, besides, is located at an angle to the molecular axis, is additionally responsible for the significant nonrigidity of the rotational HNCO spectrum, a high description accuracy requires a large set of spectroscopic constants. Our studies revealed that truncating the series used to the terms for which all the expansion coefficients are $\geq 3\sigma$ errors in absolute value is a fundamental point in the expansion of the Hamiltonians to minimize the frequency prediction errors based on the entire set of measurements. The set of constants given in Table 4 shows that the HNCO molecule has maximum nonrigidity in the states with $K_a = 0$ and particularly in $K_a = 7$ (because the vibrational state v_6 is close to $K_a = 6$). The insufficient set of spectroscopic constants used by Niedenhoff et al. (1995) can be an additional cause of the errors in the description of the HNCO spectrum. The dependence of the dipole moment on J and K_a revealed by the measurements (Shoolery et al. 1951; Shoolery and Sharbaugh 1951;

White and Cook 1967) is also independent evidence for the nonrigidity of the HNCO spectrum.

Table 6 includes the frequencies of the a-type rotational transitions for $K_a = 0$ and ± 1 that are of greatest interest in precision studies of interstellar clouds calculated using the constants from Table 4. The rms frequency uncertainties given in parentheses, including the cross-correlation between the constants, do not exceed 1 kHz (1σ) for frequencies below 500 GHz and are better than 10 kHz for all frequencies below 1.1 THz. The same errors recalculated to the Doppler velocity scale, ≤ 2 m s^{-1} in the entire measured frequency range up to 1.1 THz inclusive, are given in a separate column. A complete table of all types of transitions calculated up to $J = 75$, $K_a \leq 7$, and including all frequencies $\lesssim 1.1$ THz in increasing order and energy levels can be sent by the authors at a personal request.

As an example of radio-astronomical measurements and to demonstrate the correctness of our HNCO frequency calculation, Fig. 3 shows the profiles of the HNCO(5-4) lines in $K_a = 0$, ^{13}CO(1-0), and C^{18}O(1-0) measured with IRAM-30m simultaneously using the same receiver. All three lines are close in frequency and lie within a 500-MHz-wide passband. Additionally, the hyperfine splitting
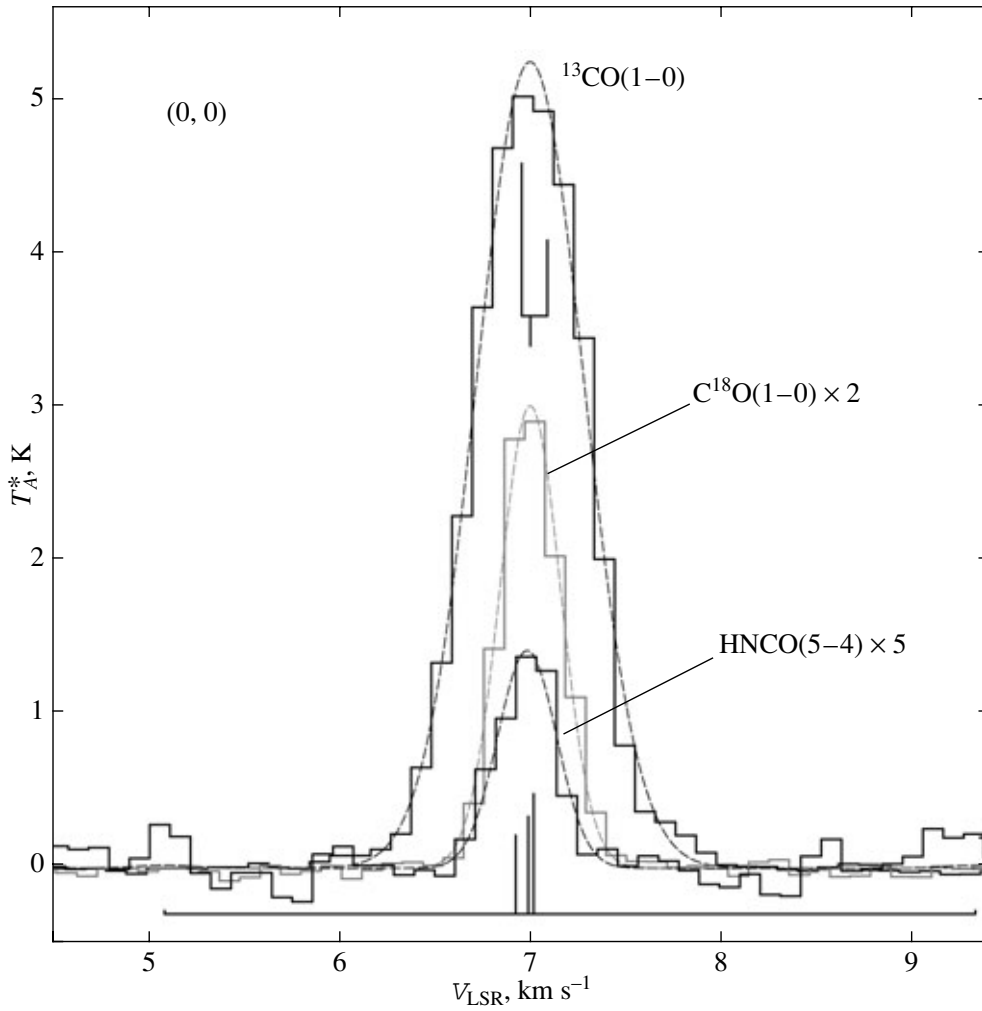
Fig. 3. Line spectra measured simultaneously in the dark cloud B217SW with IRAM-30m. The hyperfine splitting of ^{13}CO and HNCO lines is also indicated.

in ^{13}CO and HNCO, which was taken into account when fitting the Gaussian curves by the least-squares method (drawn by the dotted lines), is indicated in the figure. In addition, our fitting code also included the actual frequency dependence of the spectral response of each channel with parabolic apodization of the correlator. The spectrum was selected from many similar records owing to the absence of any detectable Doppler shift of the line centers between ^{13}CO(1−0) and C^{18}O(1−0). The laboratory frequencies of these lines determined by one of the authors of this publication based on Lamb-dip sub-Doppler spectroscopy (Cazzoli et al. 2003, 2004) have (1σ) errors recalculated to the Doppler velocity scale of 0.1 and 0.4 m s^{-1}, which are considerably smaller that the radio-astronomical measurement errors. The parameters of all three lines calculated with our code are given in Table 7. We see from this table that, to within 1σ errors, all three lines have the same Doppler velocity. If we used the HNCO(5−4) frequency calculated

using the constants from Niedenhoff et al. (1995), then the difference would exceed 5σ. The position that we chose for B217SW coincides with the center of a differentially rotating dark cloud that, besides, has additional microturbulent broadening, which we found based on detailed mapping of the source in spectral lines of many molecules. Therefore, the measured line widths corrected for the hyperfine and instrumental broadenings (due to the limited spectral resolution) is still larger than the corresponding thermal widths at $T_k = 10$ K by several times. As regards the kinetic temperature, it proved to be close to the excitation temperature for CO isotopes, $T_{ex} = 10.75$ K, estimated from the antenna temperature ratio by assuming the T_{ex} equality and the terrestrial isotopomer ratio X(^{13}CO)/X(C^{18}O) = 500/90. The optical depth in the ^{13}CO(1−0) line was found to be 1.33(4).

Table 7. Parameters of the molecular lines measured simultaneously in the dark cloud B217SW with IRAM-30m (the rms uncertainties in units of the last significant digits are given in parentheses)

Line	V_{LSR}, km s^{-1}	ΔV, m s^{-1}	$\Delta V_{10\,K}$, m s^{-1}	T_A^*, K
^{13}CO(1−0)	7.0054(15)	663(4)	126	5.48(3)
C^{18}O(1−0)	7.0047(19)	354(5)	124	1.59(2)
HNCO($5_{0,5}$−$4_{0,4}$)	6.9941(113)	332(33)	104	0.32(3)

CONCLUSIONS

We have performed laboratory measurements of rotational transitions in an HNCO molecule in the ground vibrational state at frequencies below 1.1 THz. In combination with the available data of other authors, our studies have increased significantly the accuracy of describing the rotational HNCO spectrum over a wide range of quantum numbers. The achieved (1σ) uncertainty for all a-type rotational transitions in the lower $K_a = 0, 1$ states does not exceed 1 kHz for frequencies below 500 GHz and is better than 10 kHz for all frequencies below 1.1 THz. Recalculated to the Doppler velocity scale, the achieved accuracy allows the velocity of the gas in star-forming regions to be determined with an absolute error of ≤ 2 m s^{-1} over the entire frequency range up to 1.1 THz inclusive. This is particularly topical in connection with the putting into operation of the ALMA (Chili) and SMA (Hawaii) submillimeter interferometers designed for operation at frequencies up to 900 GHz. Moreover, the achieved improvement of the laboratory HNCO frequencies has already been successfully used in measuring the internal motions in several tens of dark clouds using spectral lines of various molecules and in improving the frequencies of laboratory-unstable molecules based on radio-astronomical observations, which will be discussed in detail in subsequent publications.

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