ROTATIONAL SPECTRUM OF THE FORMYL CATION, HCO⁺, TO 1.2 THz

Valerio Lattanzi,[1,2] Adam Walters,[2] Brian J. Drouin, and John C. Pearson
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099
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ABSTRACT

A variety of high-quality spectroscopic studies have contributed to knowledge of the formyl cation, HCO⁺, and its rare isotopologues, but technical limitations have previously limited precise determinations of the far-infrared, or terahertz spectrum. This study extends the microwave, millimeter, and submillimeter spectroscopy of HCO⁺ into the terahertz range. The resulting measurements and predictions are of sufficient coverage to adequately address astrophysical questions about this species using the *Herschel Space Observatory* or the Atacama Large Millimeter Array.

Subject headings: catalogs — ISM: molecules — methods: laboratory — molecular data —
solar system: formation

1. INTRODUCTION

HCO⁺ is an ubiquitous and abundant molecule in the interstellar medium, observable in a multitude of different objects. Examples include proto–planetary nebulae (Sánchez Conteras & Sahai 2004), the envelope around a T Tauri star (Qi et al. 2003), giant molecular clouds such as Orion (Snyder et al. 1977), photodissociation- and photon-dominated regions (Young Owl et al. 2000; Savage & Ziurys 2004), massive star-forming regions (Purcell et al. 2006), molecular outflows (Girart et al. 2000), dense regions in a diffuse cloud around Cygnus OB2 (Scappini et al. 2000), the dense cores of the Galactic circumnuclear disk (Cristopher et al. 2005), comets (Milam et al. 2004), and the diffuse interstellar medium (Liszt & Lucas 2004). HCO⁺ emission has also been observed toward external galaxies both in nuclei (Liszt & Lucas 2004; Seaquist & Frayer 2000) and disks (Brouillet et al. 2005 and references therein) and at high-redshift ($z > 2$; Riechers et al. 2006). It is a key molecule for astrophysics, because it has a relatively large abundance and large dipole moment and therefore is used as a tracer of high-density molecular gas. Chemical models suggest that HCO⁺ plays an important role in the chain of reactions leading to complex organic molecules. Rotational lines of vibrationally excited HCO⁺ may be observed in hot or highly excited objects. The lowest energy vibration is that of the bending state at 828.2 cm⁻¹. Lines of the different isotopomers can also be observed in astrophysical spectra. The emission of the deuterium isotopomers can be anomalously strong due to enhanced deuterium fractionation (Guilloteau et al. 2006), and study of double isotopically substituted species containing deuterium is also interesting.

The formyl cation was detected in the interstellar medium as Xogen (Buhl & Snyder 1970) before being identified in the laboratory. Then, in 1975, the ground rotational transition was detected by microwave spectroscopy (Woods et al. 1975). Finally, its rovibrational spectrum was observed by infrared laser spectroscopy in 1983 by Gudeman et al. (1983). No measured electronic spectrum of this species has been reported. Since its initial identification, rotational spectra of the formyl cation have been reported numerous times. The first studies (Woods et al. 1975;

Bogey et al. 1981; Sastry et al. 1981) each used the DC discharge of low-pressure molecular hydrogen and carbon monoxide. The rotational spectrum of HCO⁺ in the ground vibrational state was recently remeasured by Savage & Ziurys (2005), who used an AC discharge to eliminate any systematic Doppler-shifted offsets. They also measured two new lines, extending the highest precision measurements up to 624 GHz. Previously, van den Heuvel & Dymanus (1982) had measured three far-infrared transitions up to 1070 GHz with lower experimental accuracy, estimated around 1 MHz.

With the launch of the *Herschel Space Observatory* (Pilbratt et al. 2001), planned in 2008, the far-infrared spectral region will be opened for astrophysical spectroscopy. In particular, the high spectral resolution instrument HIFI will operate in a range from about 480 to 1910 GHz. With its high resolution ($R = 5 \times 10^6$) it will be possible to unambiguously identify molecular species. Study of higher rotational transitions of HCO⁺, compared to, for example, HCN, will help separate the effects of chemical, versus excitation, processes (Young Owl et al. 2000). However, just as at lower frequencies, very accurate transition frequencies will be required.

In order to facilitate identification, and for modeling purposes, very accurate rest frequencies (ideally 10 kHz) are often essential for astrophysics. The precise laboratory measurement of the spectra of ions is challenging in many aspects. For example, measurements of the spectra of ions in the laboratory may suffer from Doppler shifts due to ion drift in the electric field of the discharge used for production. The offset depends highly on discharge conditions that cannot be maintained perfectly constant during measurement. Therefore, postmeasurement correction of these systematic shifts is difficult. A double-pass setup was used for this experiment to average the Doppler offset of the rotational line centers. This arrangement has also been used in recent measurements of DCO⁺ (Caselli & Dore 2005).

A molecular substitution structure has been calculated by Woods et al. (1975), who measured the $J = 0–1$ transition of the parent species and five isotopomers as well as the $J = 1–2$ transition of DCO⁺. A further 14 lines in the 140–360 GHz range were measured by Bogey et al. (1981), who were hence able to derive quartic Hamiltonian parameters and take the centrifugal distortion into account in their structural analysis. Subsequently, Plummer et al. (1983) measured the $J = 2–3$ transition of HC¹⁸O⁺ and HC¹⁷O⁺. Caselli & Dore (2005) have recently provided very precise laboratory data on the deuterated isotopomers DCO⁺,

[1] Department of Physics, University "La Sapienza," P.le Aldo Moro 2, Rome, Italy.
[2] Centre d'Etude Spatiale des Rayonnements, Toulouse University, CESR, 9 avenue du Colonel Roche, Boite postale 4346, 31028 Toulouse Cedex 4, France; adam.walters@cesr.fr.

DC^{18}O$^+$, and D^{13}CO$^+$ in the 137–792 GHz region, which allowed the first determination of the sextic centrifugal distortion parameters for these species. They also reported a measurement by radio astronomy of the ground rotational transition of DCO$^+$, which showed for the first time a hyperfine splitting due to the deuteron and were hence able to determine the quadrupole coupling and spin rotation parameters of the molecule. This was possible because of the low Doppler line widths in cold quiescent clouds. Similarly, Schmid-Burgk et al. (2004) fitted two magnetic hyperfine components to the first rotational transition of H^{13}CO$^+$ observed in a dark cloud. This work enables calculation of parameters for the nuclear spin Hamiltonian. They also reported ab initio calculations of this coupling parameter for both the latter species and for HC^{17}O$^+$ and HC^{18}O$^+$.

Laboratory measurements have also been made of rotational transitions within excited vibrational states. Blake et al. (1987) used far-infrared laser sideband spectroscopy to measure two rotational transitions in the ground vibrational state and three in the first bending mode (01^{1}0), allowing a determination of the l-type doubling parameter and one related centrifugal parameter. Rotational transitions of HCO$^+$ and DCO$^+$ in the ν_1, ν_2, $2\nu_2$, and ν_3 vibrational states were measured by Hirota & Endo (1988) in the 216–358 GHz range. Detailed work on DCO$^+$ was carried out by Dore et al. (2003), who measured transitions up to $J = 4$ in the bending overtone states up to $\nu_2 = 4$. They reported a Coriolis-type interaction between the $\nu_1\nu_2^l\nu_3 = 01^11$ and 10^00 states. These measurements were later completed to include bending satellites with high values of the vibrational angular momentum up to $l = 3$ (Caselli & Dore 2005). Foltynowicz et al. (2000) have reported results on the second overtone of the HCO$^+$ bend yielding a new determination of the harmonic bending frequency and the first measurement of anharmonicity in the bending mode.

The first infrared measurement was that of the ν_1 stretching vibration (Amano 1983), which was followed up by Owtrusky et al. (1989). Spectral analyses have also been reported for the ν_3 stretching vibration (Foster et al. 1984; Davies & Rothwell 1984), the ν_2 bending vibration (Davies et al. 1984; Kawaguchi et al. 1985), and several hot bands (Liu et al. 1988).

2. EXPERIMENTAL DETAILS

The measurements reported here were carried out at the Jet Propulsion Laboratory (JPL). An amplified millimeter-wave module, with 10–100 mW of output power, and a series of commercial (Virginia Diodes) and JPL-built multiplier chains were used to produce terahertz radiation. The radiation source was a sweep synthesizer phase locked to a frequency standard good to 1 part in 10^{12}, so frequency errors depend entirely in determining line center of the absorption profile, which were measured in both increasing and decreasing frequency and averaged. Toneburst modulation (100 kHz tone, 0.5 kHz burst, 0.10–0.15 V amplitude) was used at magnitudes that matched the 0.5–1.5 MHz line widths. A tunable YIG filter was used for suppression of spurious harmonics. In the rest of this article we refer to the complete setup of synthesizer, filter, millimeter module, and amplifier as "the source." Further details of the spectrometer system are described in detail elsewhere (Drouin et al. 2005; Maiwald et al. 2005).

HCO$^+$ ions were produced in a cooled 1 m glass cell using a DC discharge at 90 mA. A flow system was used in which the gas samples and the vacuum pump represent the input and output respectively. The cell was regulated to 240 K with methanol cycled through a N$_{2(l)}$ heat exchanger. In order to maintain good signal for HCO$^+$, a mixture of molecular hydrogen at $P_{\mathrm{H}_2} = 75$ mtorr and carbon monoxide at $P_{\mathrm{CO}} = 3$ mtorr was used. For the rare isotopomers, molecular deuterium or ^{13}CO, or both, were used
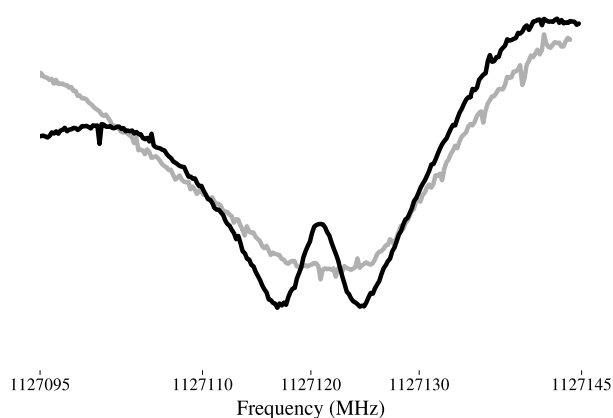

FIG. 1.—Spectral measurement of H^{13}CO$^+$. The feature only appears within a discharge of H$_2$ and enriched ^{13}CO; a scan with no ^{13}CO is shown in gray.

at similar pressures as the main isotopologues. A sample spectrum is shown in Figure 1. A double pass of the microwave radiation through the cell was used to increase sensitivity and to average any Doppler shift due to ion drift in the discharge. This was achieved using a polarizing beamsplitter, aligned in parallel polarization to the source radiation, and at 45° to the quasi-optical beam path between the source and the cell. A rooftop reflector at the opposite end rotates the polarization by 90° and reflects back through the cell toward the beamsplitter, which reflects the beam into a composite Si bolometer cooled to 2.1 K with pumped ^{4}He liquid. The detector response was passed through a preamplifier, demodulated by a lock-in amplifier at 0.5 kHz, and digitized for storage and treatment by computer. Typically, a single, strong, well-predicted transition was first measured, when the source was modified for a different frequency band, to determine appropriate sample pressure and modulation depth before subsequent measurements were made.

3. ANALYSIS

A separate fitting analysis for each isotopomer was performed, using the SPFIT and SPCAT programs[3] (Pickett 1991) to fit and generate improved predictions up to 3000 GHz. These predictions are given as supplementary material and fitting files are available online at the JPL catalog site[4] (Pickett et al. 1998). We estimate our uncertainties as 30–100 kHz, for all the measured transitions. For each species we present the lines used in the analysis, the determined molecular parameters, and make comparisons to previous work.

In the following we use the term "microwave" to generally describe all data (millimeter, submillimeter, and terahertz) taken using microwave techniques of a phase-locked source, regardless of the source being a fundamental oscillator or harmonically generated radiation. When several measurements were available for the same transition we recommend a "best" one according to criteria discussed later.

3.1. HCO$^+$

In order to search for new lines, we first made predictions from a fit of all previous microwave (Woods et al. 1975; Bogey et al. 1981; Savage & Ziurys 2005; Blake et al. 1987; Sastry et al. 1981; Hirota & Endo 1988; van den Heuvel & Dymanus 1982) and infrared (Davies & Rothwell 1984; Davies et al. 1984; Kawaguchi

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[3] See also http://spec.jpl.nasa.gov.
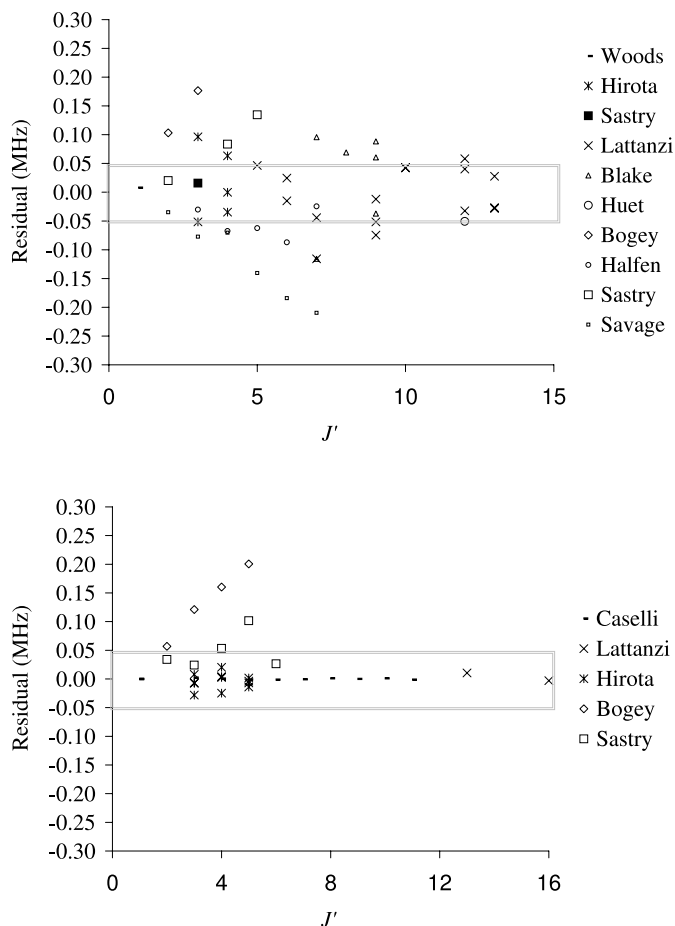[4] See also http://spec.jpl.nasa.gov.

FIG. 2.—Residuals of HCO+ fit (*top*) and DCO+ fit (*bottom*) for measured transitions. Transitions excluded from the analysis are given open symbols; the box represents ±50 kHz from model. Most studies report 100 kHz or less error.

et al. 1985; Foster et al. 1984; Gudeman et al. 1983; Amano 1983; Liu et al. 1988) measurements. Once the data set was compiled, some critical evaluation of available literature data proved necessary. After reconciling systematic offsets in several different microwave ground-state data sets, the best transitions were chosen for inclusion in a multistate analysis.

An evaluation of the ground-state data was necessary due to incompatibilities associated with the treatment of the ion drift–induced Doppler shift and/or frequency calibration errors. Bogey et al. (1981), Sastry et al. (1981), and Savage & Ziurys (2005) each discuss the phenomenon; however, the method of cancellation of the effect is different in each case, as well as the results. The present work offers a third method, that of a double-pass quasi-optical beam path, which leads to good agreement with Sastry et al. (1981). This method is arguably similar to that used by Sastry et al. (1981) for the J = 3–2 transition.

The magnitude of the disagreement between the prior results can be seen from inspection of Figure 2 to be from 50 to 250 kHz. The linear divergence from the present data fit is evident in each study that measures two or more transitions, (a zero residual corresponds to the present, best fit). The deviations are of the same order as the velocity correction derived by Sastry et al. (1981). After discussing these differences with the Arizona group a more accurate set of measurements (D. T. Halfen & L. M. Ziurys 2006, private communication) were made, which are in good agreement with Sastry et al. (1981) and the present work. This was accomplished through remeasurement, in the same AC discharge system, with a new synthesizer that is calibrated to 1 part in 10^9.

Nevertheless, the high precision of the Savage & Ziurys (2005) AC measurements is evident in the tight linearity of the residuals representing this data in Figure 2. The evidence is all consistent with a small, but entirely reasonable, offset in the fundamental oscillator used for the measurements of Savage & Ziurys (2005). Finally, returning to the original submillimeter data from Sastry et al. (1981), the additional data from this study reveals that the correction applied therein is likely to be underestimated, since even the corrected transition frequencies above $J' = 3$ move systematically away from the "trust" region denoted by the ±50 kHz box drawn about the residual zero line in Figure 2. It should also be noted that velocity offsets, as well as frequency calibration issues, can each lead to the inconsistencies observed in the HCO+ data sets.

In the best fit there is an assumption that the double-pass arrangement used in this experiment completely averages the two Doppler components of the ion signal. Since the present data set is the only high-precision work at high J, there is no practical way to verify this assumption. However, the excellent agreement in the DCO+ data indicate that the assumption is valid up through 800 GHz. In the multistate fits used for final predictions the "best" microwave data was fitted along with new measurements. Lines were weighted using previously quoted experimental error. The microwave fit includes data from the ground, first, and second vibrationally excited bending states (01¹0 and 02⁰0). The multistate fit also includes additional data for both of the stretching vibrations (100 and 001). The complete set of fitted ("best") microwave measurements is shown in Table 1. The residual signifies observed − calculated frequency differences with the fit. Following the notation used in the JPL online catalog (and that used in SPFIT), we indicate $v = 0$ as the ground vibrational state, $v = 1$ as the first bending mode (ν_2 or 01¹0) with $l = \pm 1$, $v = 2$ is (2ν_2 or 02⁰0), $v = 3$ as the C−O stretch mode (ν_3 or 001), and $v = 4$ is the C−H stretch mode (ν_1 or 100). For predictions the $v = 5$ state represents the as yet unobserved (02²0) state, which was approximated during fitting of 02⁰0 using fixed values for $-q/2$ and $-q_J/2$ (multiplied by $\sqrt{2}$ for SPFIT) assumed from the 01¹0 state.

The rotation of the molecule splits the two degenerate bending modes by the different coupling of the angular and vibrational velocity vectors (Coriolis force). Allowing for the above splitting, the rotational frequencies are fit to

$$\nu = B_0 J(J+1) - D_0 J^2(J+1)^2 + H_0 J^3(J+1)^3 \quad (1)$$

for the ground vibrational state, with

$$\nu^\pm = B_1\left[J(J+1) - l^2\right] - D_1\left[J(J+1) - l^2\right]^2 + H_1\left[J(J+1) - l^2\right]^3 \pm \frac{q'}{2}J(J+1) \pm \frac{q'_J}{2}J^2(J+1)^2 \pm \frac{q'_{JJ}}{2}J^3(J+1)^3 \quad (2)$$

for the vibrationally excited bending states and as in equation (1) for the other vibrational states. The terms B_i, D_i, and H_i are the rotational and distortional parameters in the corresponding vibrational state, l is the vibrational bending angular momentum, q' is the l-type doubling parameter, and q'_J and q'_{JJ} are its centrifugal distortion corrections. The primes on the q-parameters indicate that SPFIT does not implicitly include the expectation values of the l-doubling wave function, such that $q' = \langle l|q|l'\rangle$. The parameters obtained from the fits are listed in Table 2.

TABLE 1
Measured Rotational Transitions Used in the Final Analysis of HCO$^+$

J'	l'	v'	J	l	v	Frequency (MHz)	Ref.	Residual (MHz)	Uncertainty (MHz)
1	0	0	0	0	0	89188.5230	1	0.00789	0.020
3	0	4	2	0	4	265434.3340	2	0.00086	0.041
3	0	3	2	0	3	265790.2470	2	0.00045	0.039
3	0	0	2	0	0	267557.6190	3	0.01571	0.050
3	−1	1	2	1	1	267418.7196	2	0.09638	0.030
3	0	2	2	0	2	268589.3045	2	0.00000	0.117
3	1	1	2	−1	1	268688.8696	2	−0.05148	0.030
4	1	1	3	−1	1	356548.7606	2	−0.03458	0.030
4	0	2	3	0	2	358098.5513	2	0.00000	0.061
4	−1	1	3	1	1	358242.4092	2	0.06334	0.030
5	0	0	4	0	0	445902.9080	4	0.04661	0.050
6	1	1	5	−1	1	534783.0698	4	0.02466	0.050
6	0	0	5	0	0	535061.5712	4	−0.01495	0.050
7	−1	1	6	1	1	623882.9970	4	−0.11569	0.050
7	0	0	6	0	0	624208.3453	4	−0.04430	0.050
9	−1	1	8	1	1	802039.1040	4	−0.01204	0.050
9	0	0	8	0	0	802458.2170	4	−0.05145	0.050
9	1	1	8	−1	1	805845.6250	4	−0.07460	0.050
10	0	0	9	0	0	891557.3993	4	0.04208	0.050
10	−1	1	9	1	1	895319.3051	4	0.04307	0.050
12	1	1	11	−1	1	1069132.8477	4	0.05831	0.050
12	0	0	11	0	0	1069693.8910	4	0.04026	0.050
12	−1	1	11	1	1	1074202.8123	4	−0.03235	0.050
13	−1	1	12	1	1	1158118.5788	4	−0.02662	0.050
13	0	0	12	0	0	1158727.2266	4	−0.02826	0.050
13	1	1	12	−1	1	1163608.7748	4	0.02761	0.050

Notes.—Here $v = 0$ is the ground vibrational state, $v = 1$ the first bending mode (ν_2 or 01^10) with $l = \pm 1$, $v = 2$ is ($2\nu_2$ or 02^00), $v = 3$ the C—O stretch mode (ν_3 or 001), and $v = 4$ is the C—H stretch mode (ν_1 or 100). Infrared data from Amano (1983), Davies & Rothwell (1984), Davies et al. (1984), Kawaguchi et al. (1985), and Foster et al. (1984) were also used in the fit.
References.—(1) Woods et al 1975; (2) Hirota & Endo 1988; (3) Sastry et al. 1981; (4) This work.

TABLE 2
Parameters for HCO$^+$

Parameter	All[a]	All Previous[b]
B_0	44594.4230(44)	44594.4316(38)
D_0	−0.082724(49)	−0.083028(92)
$H_0 \times 10^6$	−0.341(156)	1.01(72)
$B(\nu_2 = 1)$...........................	44677.1489(18)	44677.1498(34)
$D(\nu_2 = 1)$...........................	−0.0844555(69)	−0.084394(87)
$E(\nu_2 = 1) \times 10^{-7}$	2.48297353(70)	2.48297364(75)
$q'/2$ ($\nu_2 = 1$).....................	105.87248(263)	105.8554(58)
$q'_J/2$ ($\nu_2 = 1$) $\times 10^3$	−0.791(32)	−0.115(223)
$q'_{JJ}/2$ ($\nu_2 = 1$) $\times 10^6$	−0.295(107)	−3.84(149)
$B(\nu_2 = 2)$[c]	44767.989(46)	44767.989(46)
$D(\nu^2 = 2)$[c]	−0.08618(150)	−0.08618(150)
$B(\nu_3 = 1)$...........................	44299.8687(78)	44299.8612(97)
$D(\nu_3 = 1)$	0.08301(21)	0.08260(38)
$E(\nu_3 = 1) \times 10^{-7}$	6.54731788(150)	6.54731718(155)
$B(\nu_1 = 1)$...........................	44240.6140(166)	44240.6129(166)
$D(\nu_1 = 1)$...........................	−0.08656(82)	−0.08651(83)
$E(\nu_1 = 1) \times 10^{-7}$	9.25980841(70)	9.25980838(70)
σ	0.046	0.396

Note.—One standard deviation in units of the last decimal place is given in parentheses.
[a] Fit including new data and selected literature data as discussed in text.
[b] Global fit of previous data.
[c] The parameters q' and q'_j for the $\nu_2 = 2$ state were fixed at $\nu_2 = 1$ values.

From merging all the available data, there are 18 well-determined parameters for HCO$^+$. Comparing the fit based on the old data and that based on the new set, it can be seen how the quartic $D(\nu_2 = 1)$ parameters are better determined. The l-type doubling distortion parameter q'_J, previously undetermined, is now determined. The marked improvement in the l-doubling parameters is essentially due entirely to the new measurements of the first bending mode ($01^{\pm1}0$), but the simultaneous vibrational analysis also helps the statistics. Table 1 shows the best-fit data, and Figure 2 shows residuals of all available microwave data sets compared to the present best fit. Parameters from the "best-fit" analysis and an "all-inclusive" analysis are given in Table 2.

3.2. Rare Isotopologues

This work includes seven newly measured lines for H^{13}CO$^+$ as well as two new measurements at higher frequency for each of the deuterated species. We performed a weighted, rovibrational analysis, including most previous measurements for DCO$^+$. For H^{13}CO$^+$ and D^{13}CO$^+$, only data for the ground vibrational state was fitted to two or three molecular parameters, respectively. For DCO$^+$, measurements made by Caselli & Dore (2005), Hirota & Endo (1988), Kawaguchi et al. (1985), and Davies & Rothwell (1984) were included in the analysis. For the D^{13}CO$^+$ species, we used lines from Caselli & Dore (2005) and from Woods et al. (1975). For the H^{13}CO$^+$ species we used lines from Schmid-Burgk et al. (2004), Bogey et al. (1981), and Gregersen & Evans (2001).

TABLE 3
Rotational Transitions for DCO⁺

$J'(F')$	l'	v'	$J(F)$	l	v	Frequency (MHz)	Ref.	Residual (MHz)	Uncertainties (MHz)
1(0)	0	0	0(1)	0	0	72039.2413	1	−0.00009	0.0073
1(2)	0	0	0(1)	0	0	72039.3028	1	−0.00030	0.0061
1(1)	0	0	0(1)	0	0	72039.3504	1	−0.00022	0.0067
3	0	1	2	0	1	214748.9960	2	0.00804	0.0190
3	0	3	2	0	3	214874.0810	2	−0.02821	0.0180
3	0	0	2	0	0	216112.5822	1	0.00227	0.0050
3	−1	2	2	1	2	216181.5872	2	−0.00668	0.0057
3	1	2	2	−1	2	217207.5090	2	−0.00760	0.0062
4	0	1	3	0	1	286326.7670	2	−0.02475	0.0290
4	0	3	3	0	3	286492.6080	2	0.02043	0.0140
4	0	0	3	0	0	288143.8583	1	0.00062	0.0050
4	1	2	3	−1	2	288235.7892	2	0.00247	0.0030
4	−1	2	3	1	2	289603.4815	2	0.00422	0.0040
5	0	1	4	0	1	357900.1470	2	0.00170	0.0130
5	0	3	4	0	3	358105.7270	2	−0.00369	0.0110
5	0	0	4	0	0	360169.7783	1	−0.00115	0.0050
5	−1	2	4	1	2	360284.5328	2	−0.01405	0.0121
5	1	2	4	−1	2	361993.8215	2	−0.00682	0.0086
6	0	0	5	0	0	432189.0052	1	−0.00135	0.0050
7	0	0	6	0	0	504200.1999	1	−0.00054	0.0050
8	0	0	7	0	0	576202.0239	1	0.00107	0.0050
9	0	0	8	0	0	648193.1357	1	−0.00001	0.0050
10	0	0	9	0	0	720172.2024	1	0.00107	0.0100
11	0	0	10	0	0	792137.8811	1	−0.00122	0.0100
13	0	0	12	0	0	936023.7532	3	0.01041	0.0500
16	0	0	15	0	0	1151718.7350	3	−0.00286	0.0500

Note.—Infrared data from Kawaguchi et al. (1985) and Davies & Rothwell (1984) were also used in the fit.
References.—(1) Caselli & Dore 2005; (2) Hirota & Endo 1988; (3) This work.

3.2.1. Deuterated Species

Both DCO⁺ and D¹³CO⁺ have recently been measured and analyzed by Caselli & Dore (2005). In their work they recorded lines in the 137–792 GHz range and determined three molecular Hamiltonian parameters for each species. For clarity, the data

TABLE 4
Spectroscopic Parameters for DCO⁺

Parameter	This Work (MHz)	Previous Work[a] (MHz)
B_0	36019.76763(41)	36019.76765(14)
D_0	0.0557956(46)	0.0557960(22)
$H^b \times 10^6$	0.0522(157)	0.054(11)
$1.5eQq$	0.2216(212)	0.2217(53)
$C_I \times 10^3$	−1.60(315)	−1.59(78)
$E(\nu_1 = 1)$.........................	77483235.2(170)	
$B(\nu_1 = 1)$.........................	35792.3325(46)	
$D(\nu_1 = 1)$	0.046361(100)	
$B(\nu_2 = 1)$	36116.79449(106)	
$D(\nu_2 = 1)$	0.0575167(314)	
$q'/2(\nu_2 = 1)$.....................	−85.51015(106)	
$q'_J/2(\nu_2 = 1) \times 10^3$	0.9214(314)	
$E(\nu_3 = 1)$.........................	57082391.7(125)	
$B(\nu_3 = 1)$.........................	35813.3520(35)	
$D(\nu_3 = 1)$	0.055580(79)	
σ	0.010	

Note.—This single sextic distortion parameter was fit for all vibrational states simultaneously. One standard deviation in units of the last decimal place is given in parentheses.

[a] Data from Caselli & Dore (2005) is weighted as states in the paper, producing *different* parameter uncertainties than reported there.

reported by Caselli & Dore was reanalyzed to obtain identical residuals to those they reported. The values of the parameters were also identical, but the predicted errors were significantly higher. We noticed that the reduced error,

$$\sigma_{\rm red} = \left[\frac{\sum (\text{Residual/Error})^2}{\text{Number of lines}} \right]^{1/2},$$

was very small due to the small residuals, below 1 kHz. This suggested the quoted uncertainty on the transitions was large compared to the random error of the fitting model. When the transition

TABLE 5
Transitions for D¹³CO⁺

J''	J'	Frequency (MHz)	Ref.	Residual (MHz)	Uncertainties (MHz)
1	0	70733.2180	1	0.0130	0.050
3	2	212194.4920	2	0.0026	0.005
4	3	282920.0055	2	0.0008	0.005
5	4	353640.3923	2	−0.0009	0.005
6	5	424354.3718	2	−0.0018	0.005
7	6	495060.6646	2	−0.0003	0.005
8	7	565757.9861	2	0.0014	0.005
9	8	636445.0518	2	−0.0013	0.005
10	9	707120.5885	2	−0.0002	0.015
11	10	777783.3159	2	0.0049	0.050
13	12	919065.1840	3	0.0560	0.050
16	15	1130859.8531	3	−0.0160	0.100

References.—(1) Woods et al. 1975; (2) Caselli & Dore 2005; (3) This work.

TABLE 6
Spectroscopic Parameters for $D^{13}CO^+$

Parameter	This Work (MHz)	Previous (MHz)
B..............................	35366.70960(47)	35366.70968(14)
D..............................	0.0534069(60)	0.05340835(266)
$H \times 10^6$......................	0.0416(247)	0.048(16)
σ	0.0173	0.004

Note.—One standard deviation in units of last decimal place is given.

TABLE 8
Spectroscopic Parameters for $H^{13}CO^+$

Parameter	This Work (MHz)	Previous (MHz)
B..	43377.3019(17)	43377.3011(27)
D..	0.0784070(79)	0.07837(39)
σ_{red}..............................	0.44588	0.62077
σ	0.297	0.493

Note.—One standard deviation in units of last decimal place is given. The previous data used are from Schmid-Burgk et al. (2004).

frequency uncertainties are reduced to obtain a reduced error close to unity, one should obtain the same errors for the model parameters as depicted in Caselli & Dore (2005). In this work we chose to use the quoted uncertainties of the transitions in our full analysis; therefore, errors for the parameters are actually *larger* than those quoted by Caselli & Dore. Tables 3–6 compare our fit of the previous data with the fit including the new measured lines. It is worth pointing out that the combined fit has very good agreement, as evidenced by the very low residuals, and that the two analyses are only significantly different in the treatment of errors, which will impact the confidence of model extrapolations.

Since overlapping data for DCO^+ and $D^{13}CO^+$ have been taken by two different experimental setups near 800 GHz, most possibilities for systematic error are remote. For DCO^+ the quadrupole-coupling eqQ and spin-rotation C_I parameters of the D nucleus are also determinable from literature data. Not surprisingly, these parameters are not improved by our new high-frequency data, since no splittings were observed.

3.2.2. $H^{13}CO^+$

A lack of high-resolution laboratory data has, until now, excluded a precise spectral characterization of this species. In the CDMS online catalog[5] (Müller et al. 2005), the reported predictions are based on the analysis by Schmid-Burgk et al. (2004), which includes data from Gregersen & Evans (2001). These predictions have an uncertainty of over 1 MHz above 700 GHz, and over 20 MHz around 2 THz. Surprisingly, the new measurements (Table 7) are in better agreement with older predictions in the JPL database (Pickett et al. 1998), which show a difference not greater than 50 kHz with the present measurements. In Table 8 the data used to obtain the two spectroscopic parameters

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[5] See also http://www.ph1.unikoeln.de/vorhersagen/.

TABLE 7
Transitions for $H^{13}CO^+$

J''	J'	Frequency (MHz)	Ref.	Residual (MHz)	Uncertainties (MHz)
1	0	86754.2884	1	−0.0018	0.0046
2	1	173506.7820	2	0.0835	0.080
3	2	260255.3390	3	−0.0044	0.035
5	4	433733.8327	4	0.0173	0.050
6	5	520459.8843	4	−0.0052	0.050
8	7	693876.2612	4	0.0084	0.050
9	8	780562.8120	4	0.0127	0.050
10	9	867232.4263	4	0.0164	0.050
11	10	953883.1712	4	−0.0317	0.050
13	12	1127120.8128	4	0.0041	0.050

References.—(1) Schmid-Burgk et al. 2004; (2) Bogey et al. 1981; (3) Gregersen & Evans 2001; (4) This work.

is listed. The new fit leads to a significant improvements on the uncertainty of B and 2 orders of magnitude improvement for D. Attempts were made to fit the sextic centrifugal distortion parameter, but it was not well defined, and the fit was not improved.

4. DISCUSSION

The present work provides newly measured rest frequencies for one of the most important astrophysical molecules in the operating range of *Herschel* HIFI, a higher frequency than that usually available from Earth-based telescopes. Our aim has been to provide predictions that can be used with confidence up to the highest frequencies available with HIFI (around 1.9 THz).

These measurements illustrate some data and analysis issues. The first is that systematic errors in laboratory experiments can make extrapolation of predictions to higher frequency hazardous, even when measurements have very low uncertainty and fit well. This problem is graphically indicated in Figure 2. The J-value corresponding to the top of the HIFI range is around 20. It can be seen from the slope (deviation vs. J) of some of the data sets that predictions which extrapolate above $J = 15$ would have systematic errors of over 1 MHz. In laboratory measurements of ions, there is a specific difficulty relating to Doppler shift in the electric field of the discharges used to create the ions, but systematic errors may also be present in measurements of any species due, for example, to absolute frequency calibration. A similar extrapolation problem arises when limited data sets lead to apparently precise, but possibly offset, predictions based on an insufficient number of determinable molecular parameters. All the recent measurements taken on HCO^+ can be considered as good in the sense that they have measured errors of order (or less than) 100 kHz, a level usually acceptable for spectroscopic purposes. It is the extrapolation to higher frequencies that may induce errors outside of the supposed statistical uncertainty. Hence, the spectra of as many species as possible should be measured over the range of *Herschel* HIFI.

The second issue that merits stressing is the importance of comparing data sets from different experimental groups and of an open-minded consensus discussion of possible sources of error. This sort of comparison is generally the best and perhaps the only method for mitigating systematic errors. It is such a comparison that gives us confidence that our measurements of HCO^+ are not affected by a significant Doppler shift. Similarly, the tight agreement between our measurements and those of Caselli & Dore (2005) for DCO^+ and $D^{13}CO^+$ indicate that neither setup is subject to systematic errors, although it is always possible, but much less likely, that both experiments suffer from identical systematic errors. The authors are grateful to D. T. Halfen & L. M. Ziurys (2006, private communication) for rechecking measurements reported in Savage & Ziurys (2004) with the same AC discharge cell probed with a single and double-pass quasi-optical alignments. These measurements, which were essentially identical

for the two configurations, are shown in Figure 1 and demonstrate that the systematic error from Savage & Ziurys (2004) was not due to a Doppler shift. This error is believed to have been due to a small frequency offset of the crystal oscillator reference which is no longer in use in that laboratory.

Another issue is the importance of adopting a common procedure for applying experimental precision to a model to ensure that extrapolations are adequately constrained. Generally, in large data sets a well-modeled spectrum has an rms residual that reflects the uncertainty of the measurement, and a weighted fit produces a reduced rms of unity. However, care should be taken with smaller data sets that may not be statistically significant or with fits over a limited region that may use an insufficient number of molecular parameters. In this case it would seem prudent not to strive to force the reduced uncertainty to one but to obtain errors on the parameters that reflect the experimentally estimated uncertainty. Some confusion is apparent in the literature of HCO⁺, in which parameters are quoted without uncertainty or with uncertainties that represent an unweighted fit. In our efforts to understand these data sets, we reproduced fit parameters and uncertainties identical to those quoted in the respective manuscripts, but we chose, in our final analysis, to perform a weighted fit that incorporates $5-100$ kHz uncertainties on most measurements. This choice results in a reduced rms much less than unity.

A final issue is closely related to the last. Astrophysicists using spectroscopic data should be able to get a clear idea of the uncertainty of a given prediction to a given confidence factor without having to reproduce the spectral analyses themselves or consider each time all the issues stated previously. This points to presenting data in a homogeneous manner, as is strived toward by databases such as CDMS (Müller et al. 2005) and JPL (Pickett et al. 1998). Once assessed correctly, uncertainties should be able to be clearly visualized using software such as CASSIS.[6]

To summarize, the new data for HCO⁺ will be available online on the JPL spectral line catalog (Pickett et al. 1998) and can be used directly as input to software such as CASSIS to provide predictions of spectra and intensity under different conditions and to analyze observations. The catalog entry includes extrapolative predictions that extend above the frequency range of HIFI, which can be useful for the lower resolution instruments of *Herschel* at these frequencies. For the main isotopologue comparison of previous and new data sets has decreased uncertainty and increased confidence on all predictions in the range of *Herschel*. For the deuterated species, recent high-resolution higher frequency data was already available but did not exceed 800 GHz. We measured higher frequency transitions, providing an independent data set for comparison. Combining the new data with the literature data for the deuterated species, predictions were obtained with an estimated uncertainty of better than 1 part in 10^7 up to 2000 GHz. The second goal of this work concerns specifically $H^{13}CO^+$. For this species, previous predictions were based on just two rotational lines obtained from astrophysical spectra, and hence, high-resolution laboratory data were needed. With our new measurements two spectroscopic parameters are now well determined, and predictions up to 2 THz can be treated with much higher confidence.

[6] See the CASSIS Web site (A. Walters et al. 2006) at http://www.cesr.fr/ ∼walters/web_cassis/.

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