Impact of Sub-Doppler Measurements on Centrifugal-Distortion Terms: Rotational Spectrum of Methyl Fluoride Revisited

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ABSTRACT: Methyl fluoride is a prototypical symmetric-top molecule. Despite the fact that its rotational spectrum has been largely investigated, centrifugal-distortion constants were determined only up to the sextic terms. The present investigation demonstrates the importance of sub-Doppler measurements in the terahertz region not only for deriving higher-order centrifugal-distortion terms but also for revising the parameters available in the literature. The Lamb-dip technique has been exploited for obtaining sub-Doppler resolution in the 102 GHz to 1.2 THz frequency range, thus allowing for the improvement of all spectroscopic parameters. Furthermore, the hyperfine structure due to fluorine and hydrogens has been resolved, thus enabling the determination of the corresponding spin—rotation constants with an accuracy rivaling that obtained by molecular-beam electric resonance measurements and of the dipolar spin—spin coupling constants for the first time. The prediction and analysis of hyperfine structures were guided and supported by high-level quantum-chemical calculations of the parameters involved.

INTRODUCTION

Although the key role played by rotational spectroscopy in atmospheric and astrophysical studies has been well-known for decades, rather new is its extension to the terahertz domain with precision, accuracy, and sensitivity comparable to those obtainable in the millimeter-/submillimeter-wave regions. The proliferation and increased abilities of remote-sensing missions for monitoring planetary atmospheres and of astronomical telescopes for space observations have spurred the need for the knowledge of either accurate transition frequencies in the terahertz regime or their derivation based on accurate spectroscopic parameters. The last point is the topic touched upon by the present work.

Though methyl fluoride (CH₃F) is of interest only to Earth’s atmosphere studies, the reinvestigation of its rotational spectrum allowed us to point out the importance of accurate measurements, at sub-Doppler resolution, on the derivation of the centrifugal-distortion terms of the effective rotational Hamiltonian. The accurate and reliable determination of the latter parameters is a key point in the extrapolation from laboratory measurements to higher frequencies. In this respect, CH₃F has been chosen because of the limited characterization of its rotational spectrum. Despite being a molecule of interest for both experimental and theoretical spectroscopy (see ref 8 and references therein), prior to this work, its rotational parameters were known only up to the sextic terms and, from the beginning of our investigation, it was clear that they were required to be extended, improved, and in some cases revised. Furthermore, methyl fluoride is a prototypical prolate symmetric-top molecule and its potential energy surface has recently been the subject of investigations aiming at a complete vibro-rotational characterization. Nikitin et al. and Manson et al. pointed out the challenge of an accurate theoretical description of its vibrational energy levels and of the proper account of vibrational polyads and resonance couplings.

CH₃F was also chosen because of its intrinsic interest. For example, reactions involving methyl fluoride have attracted attention because of the important roles played in atmospheric and combustion chemistry (see, for example, refs 11–13 and references therein). Because the fluorinated methanes, namely CF₄ (Freon 14), CHF₃ (Freon 23), CH₂F₂ (Freon 32), and CH₃F (freon 41), are environmentally less harmful than the fully halogenated chloro-fluorocarbons (CFCs), they were suggested as their replacements. Their main impact on the environment is therefore related with global warming. On one end, CH₃F has a low global warming potential and is no longer in use today. On the other end, the atmospheric CH₄ mixing ratio has increased because of anthropogenic sources and methyl fluoride has been found to be an effective inhibitor of methane oxidation and production (see ref 15 and references therein). To understand the impact of anthropogenic activities on the environment, climate models have been developed. Most of them account for the chemical processes taking place in the atmosphere and therefore require a precise knowledge of the thermodynamic and
kinetic properties of the atmospheric reactions involved. This need led, for example, to the recent investigation of the thermochemistry of atmospherically important halomethane derivatives, also including CH₂F₂, by means of high-precision quantum-chemical calculations.

The last comments concern the most recent studies of the rotational spectrum of methyl fluoride, because some measurements will be used in the present work and they report the parameters we aim at improving. In ref 18, the submillimeter-wave spectrum of CH₂F₂ up to 1.625 THz was observed with transition frequencies retrieved in most cases with an uncertainty of 500 kHz. These measurements allowed for the first "accurate" determination of the sextic constants. Subsequently, Papousek et al. recorded the far-infrared spectrum of CH₂F₂ with an accuracy of 1.5 MHz up to ~3 THz. These data were simultaneously fit with previous rotational and vibro-rotational measurements, thus enabling the revision of the sextic terms of ref 18. The consideration of vibrorotational transitions allowed them to also determine the A₀ and D₀ constants. As will be demonstrated later in the text, the spectroscopic parameters of ref 19 turned out to be insufficiently accurate to reproduce our sub-Doppler measurements. Because the Lamb-dip technique presented here allowed us to resolve the hyperfine structure due to fluorine and hydrogens, the work by Wofsy, Muenter, and Klemperer should also be mentioned. In that study, the authors measured the molecular-beam electric resonance spectrum of methyl fluoride in several rotational states, and from the analysis of the hyperfine structures they determined the corresponding parameters, namely, the spin–rotation constants, of both fluorine and hydrogens. On the other hand, they did not account for the dipolar spin–spin parameters, which have been derived for the first time in the present study.

In passing, we mention the infrared-terahertz double-resonance spectroscopy of methyl fluoride and methyl chloride at atmospheric pressure: in ref 5 a spectroscopic tool for highly selective remote sensing of atmospheric trace polar molecular gases is presented.

![Image](image-url)

**Figure 1.** K structure (with K = 0–4) of the J = 5 ← 4 rotational transition recorded at P = 2 mTorr (modulation depth = 300 kHz). In the inset, the hyperfine structure of the K = 4 component is shown in detail (recorded at P = 0.5 mTorr, modulation depth = 15 kHz).

### EXPERIMENTAL DETAILS

Measurements were performed with a frequency-modulated computer-controlled spectrometer working from 65 GHz to 1.6 THz, with the 102 GHz to 1.58 THz frequency range actually considered. The Lamb-dip technique was employed to obtain sub-Doppler resolution and was applied in the 102 GHz to 1.2 THz frequency range. Doppler-limited measurements were carried out using a free-space cell with a single-path arrangement, whereas the double-path configuration as well as a terahertz Fabry–Perot interferometer, constructed using suitable metallic meshes, were employed in the Lamb-dip measurements (for details, the reader is referred to ref 25). Doppler-limited measurements were performed in the 1.5–1.6 THz range and for very weak transitions at frequencies below 1.2 THz.

Our spectrometer is a modification of the terahertz spectrometer described in detail refs 21 and 27. The millimeter- and submillimeter-wave sources employed, phase-locked to a rubidium frequency standard, were either frequency multipliers driven by Gunn diode oscillators or Gunn diode oscillators themselves. The frequency modulation was obtained by sine-wave modulating the 72 MHz local oscillator of the synchronizer loop. For Doppler-limited measurements, the modulation depth was varied from 100 kHz to 3.0 MHz, according to the transition frequency under consideration. For the Lamb-dip recordings, modulation-depth values ranging from 4 to 72 kHz were used. Liquid-He cooled InSb detector was used, with Schottky diode detectors also employed at frequencies below 500 GHz. In both cases, the output was processed by means of a Lock-in amplifier tuned to twice the modulation frequency, and thus performing second harmonic detection.

With respect to the experimental conditions, a commercial sample (purity >99%) was used without further purification. Doppler-limited measurements were carried out at pressure values ranging from 0.3 to 50 mTorr. For Lamb-dip measurements, low pressure values (0.1–1.2 mTorr) were chosen to minimize the dip widths as much as possible and to avoid frequency shifts.
SPECTRAL ANALYSIS

Figures 1 and 2 depict the characteristic $K$ structure of the $J = 5 \leftarrow 4$ and $J = 31 \leftarrow 30$ rotational transitions, respectively. Figure 2 makes it evident that the $K = 3n$ lines are expected to be more intense than the other ones due to the hydrogen nuclear-spin statistics. It is also worth noting the very good signal-to-noise ratio (S/N) of the observed spectra, even in the 1.57 THz region. Figure 1 shows in the inset the Lamb-dip recording of the $K = 4$ transition; the doublet observed is essentially due to the fluorine

Figure 2. $K$ structure (with $K = 0 \rightarrow 6$) of the $J = 31 \leftarrow 30$ rotational transition recorded at $P = 2$ mTorr (modulation depth = 3 MHz). In the insets, the Doppler-limited recordings of the $K = 0$ and 6 components ($P = 2$ mTorr, modulation depth = 1.8 MHz) are shown together with the corresponding predictions based on this work and on the parameters of ref 19.

Figure 3. Hyperfine structure (hfs) of the $K = 6$ component of the $J = 7 \leftarrow 6$ rotational transition recorded using the Lamb-dip technique ($P = 0.4$ mTorr, modulation depth = 10.5 kHz). Simulated and stick spectra based on computed hyperfine parameters are also shown to point out how hfs modifies by consideration of fluorine only (in blue) to the additional inclusion of hydrogens (in red). In the inset, the simulated hfs is depicted with consideration of fluorine only (dashed blue line), with consideration of fluorine and hydrogen spin–rotation constants (SR; dash-dot-dot red line), and also with inclusion of dipolar spin–spin coupling constants (SS; solid red line).

**This work parameters**

**Papousek et al. parameters**
spin--rotation interaction, with the hydrogen spin--rotation and dipolar spin--spin interactions only leading to a broadening of the observed features. The hyperfine structure shown in the inset of Figure 1 is rather representative of that shown in most of the recorded Lamb-dip spectra. In fact, the splitting due to the spin--rotation interaction increases by enlarging the value of \( K \), but actually only for a few \( K = 3 \) and 6 transitions could we observe a different hyperfine structure. Though the effective Hamiltonian used for the analysis is introduced below, we here note that Figure 3 provides an example of how the hyperfine structure evolves from the consideration of fluorine only to the inclusion of spin rotation for hydrogens and then of the dipolar spin--spin coupling terms. Hyperfine structures could be resolved up to 611 GHz; Lamb-dip measurements at higher frequencies only permitted us to retrieve very accurate transition frequencies.

The hyperfine components result from the \( \Delta F' = \Delta F = +1, 0, -1 \) selection rules, where \( F_i \) and \( F \) are the hyperfine quantum numbers coming from the coupling schemes \( F_i = F + I_F + I_n \) and \( F = F_1 + I_n \), where \( I_F \) is the nuclear spin of fluorine and \( I_n \) is the sum of the nuclear spins of the three H nuclei.

The effective Hamiltonian can be written as

\[
H = H_{\text{ROT}} + H_{\text{SR}} + H_{\text{SS}}
\]

(1)

where \( H_{\text{ROT}} \) is the rotational Hamiltonian operator for a symmetric-top molecule, including centrifugal-distortion terms up to the octics.

\[
H_{\text{SR}} = \sum_K L_K \cdot C_K \cdot J
\]

(2)

is the spin--rotation Hamiltonian written in terms of a second-rank tensor \( C_K \) coupled with the rotational and nuclear-spin momenta. The sum runs over all L nuclei of the molecule having nonzero nuclear spin (i.e., all atoms but carbon in the present case). Finally, \( H_{\text{SS}} \) is the dipolar spin--spin Hamiltonian

\[
H_{\text{SS}}^{(LM)} = I_L D_{LM} I_M
\]

(3)

with \( L \) and \( M \) denoting either H or F or H and H. The relevant dipolar spin--spin terms are \( D_{ll} \), \( D_{l2} \), and \( D_{22} \), which correspond to 0.5 times the \( D_{ll} \) (H--F) component changed in sign, to the half difference of the \( D_{yy} \) and \( D_{xx} \) components \([D_{yy} - D_{xx}] / 2\) of the H--F spin--spin tensor, and to the \( D_{xx} \) component of the H--H dipolar spin--spin coupling tensor, respectively (for the expressions of \( D_{ll} \), \( D_{l2} \), and \( D_{22} \), the reader is for example referred to refs 31 and 32).

For predicting the hyperfine pattern of the rotational spectra, we made use of the spin--rotation and spin--spin constants determined by quantum-chemical calculations, as explained in the following section. Simulations based on computed hyperfine parameters (as exemplified by the inset of Figure 3) allowed us to identify those transitions that show hyperfine structures with a sizable effect due to hydrogens.

To accurately retrieve the transition frequencies from the recorded spectra, for the distorted and/or partially blended features, we resorted to a line-profile analysis using the Lorentzian function and the Voigt profile model for Lamb-dip and Doppler-limited measurements, respectively. In all the other cases, the experimental data points were fit with a parabolic function. However, in all cases the frequency values were obtained as averages of sets of measurements. On the basis of the standard deviations of these averages, the transition intensities and the \( S/N \) we estimated the experimental uncertainties to range from 10 to 20 kHz for Doppler-limited measurements and to conservatively be 1 kHz for the Lamb-dip ones (with only a few exceptions due to the low \( S/N \)). Figure 4, which depicts the \( K = 0 \) to \( K = 2 \) components of the \( J = 22 \) \( \leftrightarrow \) 21 rotational transition, demonstrates how the full line width is reduced when going from Doppler-limited to Lamb-dip measurements (from about 4.3 MHz to \( \sim 100 \) kHz). Therefore, Figure 4 makes it evident that also in the terahertz frequency range, transition frequencies can be retrieved with an accuracy of 1 kHz by exploiting the Lamb-dip technique.
QUANTUM-CHEMICAL CALCULATIONS

Quantum-chemical calculations of the rotational, centrifugal-distortion, and hyperfine constants were carried out with the CFOUR program package. An exhaustive account on this topic can be found in refs 38 and 39, where the theoretical background and computational procedures are described in detail, but in the following we provide a brief summary of the relevant points.

To achieve the accuracy required for a quantitative prediction of the experiment, calculations were performed using the coupled-cluster singles and doubles (CCSD) method augmented by a perturbative treatment of triple excitations (CCSD(T)) in conjunction with the cc-pCV5Z basis set, with all electrons being correlated. Equilibrium parameters were computed at the semiempirical equilibrium structure derived by Demaison et al. The vibrational corrections to hyperfine parameters and rotational constants as straightforwardly derived from the equilibrium structure of ref 43. Equilibrium rotational constants as straightforwardly derived from the equilibrium structure of ref 43. Equilibrium values of the hyperfine parameters at the CCSD(T)/cc-pCV5Z level, with all electrons correlated and using the equilibrium structure of ref 43. Vibrational corrections to hyperfine parameters and quartic and sextic centrifugal-distortion constants at the CCSD(T)/cc-pCVTZ level, with all electrons correlated.

The ground-state rotational constants were derived by augmenting the equilibrium rotational constants $B_0$ (straightforwardly derived from the semiempirical equilibrium structure) for vibrational corrections $\Delta B_0$:

$$B_0 = B_0^i + \Delta B_0^i = B_0^i - \frac{1}{2} \sum r \alpha_r^i$$

where the $\alpha_r^i$ are the vibration–rotation interaction constants, with the sum running over all normal modes and $i$ denoting the inertial axis.

As concerns the spin–rotation interaction, each element of the spin–rotation tensor has an electronic and a nuclear contribution. As implemented in CFOUR, the electronic contribution was evaluated as the second derivative of the electronic energy with respect to the rotational angular momentum and the nuclear spin $I_z$ in conjunction with perturbation-dependent basis functions (usually referred to as rotational London atomic orbitals). The nuclear contribution only depends on the geometrical structure of the molecule. The expression for the components of the dipolar spin–spin coupling tensor $D_{LM}$ can be found, for instance, in refs 28, 48, and 49. They only depend on molecular structure, thus not requiring any electronic structure calculation. Quantum chemistry was employed for computing the vibrational corrections to the equilibrium values.

Vibrational corrections to both spin–rotation and dipolar spin–spin constants were obtained as the difference between the vibrationally averaged and equilibrium values. As implemented in CFOUR, vibrational averaging of properties is accomplished via an expansion of the expectation value over the vibrational-wave function in a Taylor series around the equilibrium value with respect to the normal-coordinate displacements. The cubic force field required for the vibrational averaging and for the evaluation of the vibration–rotation interaction and centrifugal-distortion constants, was obtained by computing the harmonic

<table>
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<th>this work</th>
<th>exp: only our meas$^a$</th>
<th>exp: global fit$^b$</th>
<th>theo$^c$</th>
<th>Papousek et al.$^{19}$</th>
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$^a$Values in brackets were kept fixed in the fitting procedure: $A_0$ to Papousek et al.$^{19}$ value, hyperfine parameters to computed values. Only our measurements were considered. Standard errors (as derived from the SPFIT output using Kisiel’s PIFORM code in the least significant digit(s) are given in parentheses.

$^b$Values in brackets were kept fixed in the fitting procedure: $A_0$ to Papousek et al.$^{19}$ value, hyperfine parameters to computed values. All available measurements from the literature were included in the fit. See text. Standard errors (as derived from the SPFIT output using Kisiel’s PIFORM code) in the least significant digit(s) are given in parentheses.

$^c$Equilibrium rotational constants as straightforwardly derived from the equilibrium structure of ref 43. Equilibrium values of the hyperfine parameters at the CCSD(T)/cc-pCV5Z level, with all electrons correlated and using the equilibrium structure of ref 43. Vibrational corrections to hyperfine parameters and quartic and sextic centrifugal-distortion constants at the CCSD(T)/cc-pCVTZ level, with all electrons correlated. See text. Parameters nondeterminable by fitting only pure rotational transitions. Dimensionless (weighted) standard deviation.
part in a fully analytic manner,\textsuperscript{51,52} and the cubic force constants as well as the corresponding derivatives of the considered property using finite-difference techniques.\textsuperscript{52,53}

### RESULTS AND DISCUSSION

A total of 230 distinct frequency lines were measured in the 102 GHz to 1.6 THz frequency range. The frequency values are provided in the Supporting Information, together with the fit output. The new measurements were independently fit and were included in global fit involving all previous pure rotational frequency (or wavenumber) values available up to approximately 3 THz for the vibrational ground state.\textsuperscript{18,19,25} The fits were carried out using Pickett’s SPFIT program,\textsuperscript{54,55} with each transition weighted proportionally to the inverse square of its experimental uncertainty. The obtained spectroscopic parameters are collected in Table 1 where they are compared with those by Papousek et al.\textsuperscript{19} which provides the most recent and accurate previous results for CH$_3$F, and to the hyperfine parameters by Wosfy et al.\textsuperscript{20} Quantum-chemical results are also reported.

From Table 1 it is evident that the present measurements allowed us to improve the uncertainties in the rotational and quartic centrifugal-distortion constants by 1 order of magnitude. The situation is different for the sextic centrifugal-distortion terms, because an important revision that deserves to be discussed in detail has been obtained. On the one hand, we note that the fit involving only our transitions is able to already well determine the sextics and 3 octic centrifugal-distortion terms. On the other hand, the inclusion of transition frequencies up to 3 THz permits us to improve the determination of $H_2$ and $L_1$ by reducing the corresponding uncertainties by more than 2 times and by about 4 times, respectively. For $H_{3K}$ and $H_{4K}$ the present results are larger than those of ref 19 by about 0.5\% (i.e., $\sim$4 times the standard error given in ref 19) and 2.5\% (i.e., $\sim$10 times the standard error given in ref 19), respectively. For $H_{5K}$ the present work leads to a rather different value, the latter differing by about 23 times the standard error given in ref 19. These large discrepancies are not due to the inclusion of the octic centrifugal-distortion terms in the set of determinable parameters; in fact, a global fit without their inclusion leads to values very similar to those collected in the second column of Table 1, with the corresponding fit affected by a large standard deviation ($\chi^2 = 7.8$). The discrepancy pointed out mostly derives by the inclusion of sub-Doppler measurements in the terahertz region. The improvement provided by our investigation is already evident at 1.57 THz and it is exemplified by Figure 2, which shows the recording at a Doppler-limited resolution of the $J = 31 \leftrightarrow 30$, with $K = 0$--$6$, rotational transition: a systematic deviation of $\sim$600 kHz of the line positions based on the parameters of ref 19 is observed. On the other hand, it has to be noted that the frequency values of ref 19 are usually affected by an uncertainty of 1.5 MHz. Therefore, a more significant example is provided by Figure 5, which depicts the comparison of the predictions based on our spectroscopic parameters and those based on the constants of ref 19 with the actual measurements\textsuperscript{19} for the $J = 57 \leftrightarrow 56$, with $K = 2$--$6$, rotational transition at 2.86 THz. It is evident that our predictions better reproduce the experimental data, with those based on the spectroscopic parameters of ref 19 sometimes lying outside the error interval. The overall conclusion of the discussion above is the importance of accurate measurements, possibly at a sub-Doppler resolution, to accurately and reliably determine centrifugal-distortion terms, which in turn are required for the accurate prediction of higher frequency values.

As concerns quantum-chemical results, we note that the experimental rotational constants are reproduced with an accuracy of about 0.1\% or better, and centrifugal-distortion constants show discrepancies of a few percent. $H_3$ is the parameter showing the largest deviation, $\sim$19\%, but it has to be noted that $H_3$ is about 3 orders of magnitude smaller than the other sextics. On the contrary, the computed value of $H_K$ is expected to be affected by an error of about 5--6\%, thus providing the first reliable determination for this constant.

In Table 1, the hyperfine parameters determined in the present work are compared with the computed ones and those obtained by molecular-beam electric resonance spectroscopy.\textsuperscript{20} For what concerns fluorine, it is noted not only that $C_{3N}$ compares well with the theoretical and previous experimental data but also that we improved its accuracy by reducing the uncertainty by about 4
times. Different is the situation for $C_{zz}$, for which our standard error is similar to that of ref 20, but with the corresponding value deviating from latter by about 4 times the standard deviation. Our high-level quantum-chemical calculations tends to confirm the determination of ref 20. A similar situation is observed for the $C_{zz}$ component of the hydrogen spin–rotation tensor (with $z$ corresponding to the $a$ inertial axis), but with the discrepancy reduced to about 2 times the standard error. The effect of hydrogens on the hyperfine structure is exemplified in Figure 3, which shows the hyperfine structure of the $K = 6$ component of the $J = 7 \leftrightarrow 6$ rotational transition. In addition to the recorded spectrum, simulations based on the computed hyperfine parameters are depicted. In detail, it is shown how the hyperfine structure modifies from the consideration of fluorine only to the inclusion of the spin–rotation interaction for hydrogens and the subsequent account for the dipolar spin–spin coupling. It is evident that the hyperfine structure observed is explained only once all the possible interactions are taken into account. For this reason, we could also determine in addition to $D$ and $E$ different $J$ rotational transitions. In addition to the recorded spectrum, simulations based on the computed hyperfine parameters are depicted. In detail, it is shown how the hyperfine structure modifies from the consideration of fluorine only to the inclusion of the spin–rotation interaction for hydrogens and the subsequent account for the dipolar spin–spin coupling. It is evident that the hyperfine structure observed is explained only once all the possible interactions are taken into account. For this reason, we could also determine in addition to $D$ and $E$ different $J$ rotational transitions. In addition to the recorded spectrum, simulations based on the computed hyperfine parameters are depicted. In detail, it is shown how the hyperfine structure modifies from the consideration of fluorine only to the inclusion of the spin–rotation interaction for hydrogens and the subsequent account for the dipolar spin–spin coupling.

In conclusion, our sub-Doppler measurements, carried out in the 0.2 GHz to 1.2 THz range, allowed us to improve the rotational and quartic and sextic centrifugal-distortion constants and to determine three octics for the first time. Lamb-dip measurements also permitted us to resolve the hyperfine structure due to fluorine and hydrogens, thus enabling the derivation of spin–rotation constants with an accuracy comparable to that obtainable by molecular-beam electric resonance measurements and the determination of two dipolar spin–spin coupling constants for the first time. In the prediction and analysis of the hyperfine structures, a key role was played by high-level quantum-chemical calculations of the parameters involved.

**REFERENCES**


