Comment on: “Hyperfine structure measurements of Co I and Co II with Fourier transform spectroscopy” by Fu et al. [JQSRT 2021, 107590]

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Abstract
This comment points out errors in the analysis of 61 magnetic hyperfine structure (A) constants of Co II energy levels by Fu et al. [JQSRT 2021, 107590]. The paper was published without full awareness of the extensive literature already available for Co II hyperfine A constants at the time; 57 of 58 A constants that were claimed to have been measured for the first time had already been measured by the prior work of Ding & Pickering [ApJS 2020, 251:24], who had published A constants for 292 levels of Co II. The A constant of 3d⁶4s² a⁵D₄ has been determined by Fu et al. [JQSRT 2021, 107590] for the first time to be 12.0±1.8 mK (1 mK = 0.001 cm⁻¹), which was found to agree with line profiles observed by Ding & Pickering [ApJS 2020, 251:24]. Discrepancies in 17 A constants of Fu et al. [JQSRT 2021, 107590] were found, which are likely due to the analysis of weak, experimentally unclassified transitions with Ritz wavenumbers 25453.966 cm⁻¹ and 25149.948 cm⁻¹ by Fu et al. [JQSRT 2021, 107590] for the A constants of the energy levels 3d⁷(⁵G)4s a⁵G₅ and 3d⁷(⁵P)4s c⁵P₂ respectively. Fewer transitions and poorer quality spectra analysed by Fu et al. [JQSRT 2021, 107590] are also concluded to have contributed to disagreements in the 17 A constants.

Keywords: Cobalt, Fourier Transform Spectroscopy, Hyperfine Structure, Atomic Data

1. Introduction
Fu et al. (2021) [1] had recently published magnetic hyperfine interaction (A) constants for 61 energy levels of Co II by analysing hyperfine structure (HFS) of spectral lines measured by Fourier transform spectroscopy. This paper was published in May 2021 apparently without the authors and reviewers being aware of the prior existing literature at the time, specifically, the substantial work of Ding & Pickering (2020) [2] published in December 2020, which reported A constants for 292 Co II energy levels. These include values for all Co II A constants published by Fu et al. [1], which were incorrectly claimed to have been measured for the first time, except for the energy level 3d⁶4s² a⁵D₄.

Out of the 60 A constants reported by both publications, 43 were in agreement within uncertainties. In this comment, discrepancies of the other 17 A constants are discussed from the point of view of the authors of Ding & Pickering [2]. The single new A constant published by Fu et al. [1] for 3d⁶4s² a⁵D₄ is found to agree with corresponding line profiles from the visible spectra analysed by Ding & Pickering [2], using the A constants of connecting levels published by both papers.

2. Cobalt Fourier transform spectra
Fu et al. [1] reported using 9 cobalt spectra from the National Solar Observatory (Kitt Peak, USA) historical archive (http://diglib.nso.edu/). However, these could not be found in the archive using the dates and serial numbers stated on table 1 of Fu et al. [1]. The spectrum transformation dates were likely listed instead of the dates at which the spectra were recorded. This is evident from the spectrum with index 7 on table 1 of Fu et al. [1].
of Fu et al. [1] - it was dated 1994, but its transformation date, serial number and parameters match exactly with a spectrum listed on table 2 of Lawler et al. (2018) [3], which was in fact measured in 1983 and also used by Lawler et al. [3] for Co II HFS analysis.

The parameters of spectra listed on table 1 of Fu et al. [1] indicate no spectrum in common between the set of spectra used by Fu et al. [1] and the set of spectra used by Ding & Pickering [2] for HFS analysis. Moreover, the UV spectra analysed by Fu et al. [1] were expected to have higher noise compared to those analysed by Ding & Pickering [2], due to their much wider spectral ranges and fewer interferogram co-adds.

3. Discrepancies and dependencies

All 17 energy levels with A constants in disagreement between Fu et al. [1] and Ding & Pickering [2] are listed on table 1. The first three columns specify level configuration, term label and J value. The fourth column lists level energies from Ding & Pickering [2]. The fifth column indicates the number of lines used by Ding & Pickering [2] to estimate the values and uncertainties of A constants in their publication. The sixth and seventh columns are A constant mean values and uncertainties ∆A determined by Ding & Pickering [2], values in the eighth and ninth columns are those determined by Fu et al. [1], which were converted from MHz to mK (1 mK = 0.001 cm⁻¹ = 29.979 MHz). The final column lists the difference in A constants, all of which were above discrepancies allowed by uncertainties.

Figure 1 arranges the 17 levels, labelled using term and J value, into tree diagrams showing A constant dependencies during the HFS analysis by Fu et al. [1], as indicated by table 3 of their paper. The arrows indicate which A constant would have affected the determination of another, e.g., the A constant of the first energy level of each tree affected hyperfine structure analysis for all other levels on the tree.

4. Experimentally unclassified transitions analysed

All A constants of energy levels on the largest tree of figure 1 were affected by the HFS analysis by Fu et al. [1] for the energy level 3d⁷(2G)4s a³G₅ at 21624.528 cm⁻¹. In table 3 of Fu et al. [1], the transition used to determine the A constant of this level was at Ritz wavenumber 25453.966 cm⁻¹, combining with the energy level 3d⁷(4F)4p z⁵G₆ at 47078.494 cm⁻¹. This transition has yet to be classified experimentally (see the spectrum and term analysis of Co II by Pickering et al. [4] and the observed Co II atomic transitions from the National Institute of Standards and Technology Atomic Spectra Database [5]). The transition has been predicted by R. L. Kurucz (1988) [6] with a very weak transition probability with a log gf of −3.6 (available on the Vienna Atomic Line Database [7]). In the spectra analysed by Ding & Pickering [2], only noise was visible at this wavenumber.

Similarly for the second largest tree of figure 1 the A constant of 3d⁷(2P)4s c³P₂ at 24886.400 cm⁻¹ was analysed by Fu et al. [1] using 3d⁷(4F)4p z³G₃ at 50036.348 cm⁻¹ as the combining level with the transition at Ritz wavenumber 25149.948 cm⁻¹. This transition is again not seen with an experimentally classified line and has a
Table 1: Table of 17 Co II energy levels and their inconsistent $A$ constants between results from Ding & Pickering [2] and Fu et al. [1]. 1 mK = 0.001 cm$^{-1}$.

| Config. | Term | $J$ | Energy$^a$ (cm$^{-1}$) | $N$ | $A^a$ (mK) | $\Delta A^a$ (mK) | $A^b$ (mK) | $\Delta A^b$ (mK) | Diff. (mK) |
|---------|------|----|-----------------------|----|-----------|----------------|-----------|----------------|---------|
| 3d$^8$  | $a^3P$ | 1  | 13404.321            | 2  | -3.0      | 5.0            | -11.9     | 1.6            | 8.9     |
| 3d$^7$(2G)$^4s$ | $a^3G$ | 5  | 21624.528            | 13 | 40.8      | 0.7            | 4.4       | 0.9            | 36.4    |
| 3d$^7$(2G)$^4s$ | $a^3G$ | 4  | 22009.344            | 17 | 22.7      | 0.4            | 30.8      | 5.9            | -8.1    |
| 3d$^7$(2P)$^4s$ | $c^3P$ | 2  | 24886.400            | 14 | 51.8      | 1.0            | 11.2      | 3.5            | 40.6    |
| 3d$^7$(2P)$^4s$ | $a^1P$ | 1  | 27585.138            | 4  | 26.4      | 0.9            | 15.0      | 8.7            | 11.4    |
| 3d$^7$(2H)$^4s$ | $a^3H$ | 4  | 27902.161            | 4  | 9.5       | 1.9            | -10.3     | 1.1            | 19.8    |
| 3d$^7$(2H)$^4s$ | $a^1H$ | 5  | 30567.173            | 10 | 29.9      | 1.3            | -7.6      | 0.9            | 37.5    |
| 3d$^7$(2F)$^4p$ | $z^3D$ | 1  | 52684.634            | 6  | 46.7      | 1.2            | 40.0      | 1.1            | 6.7     |
| 3d$^7$(2P)$^4p$ | $y^5D$ | 3  | 61240.746            | 4  | 8.4       | 1.6            | 5.6       | 0.9            | 2.8     |
| 3d$^7$(2G)$^4p$ | $z^3H$ | 5  | 63306.686            | 7  | 22.1      | 0.7            | 24.5      | 0.9            | -2.4    |
| 3d$^7$(2P)$^4p$ | $y^3D$ | 3  | 63586.987            | 8  | 5.6       | 1.0            | -23.4     | 3.5            | 29.0    |
| 3d$^7$(2G)$^4p$ | $z^3H$ | 6  | 63597.396            | 16 | 16.0      | 2.0            | -14.4     | 0.9            | 30.4    |
| 3d$^7$(2G)$^4p$ | $z^1G$ | 4  | 64401.359            | 8  | 22.2      | 1.1            | -23.6     | 0.9            | 45.8    |
| 3d$^7$(2P)$^4p$ | $z^3P$ | 1  | 65028.512            | 5  | 5.1       | 0.7            | -39.8     | 3.5            | 44.9    |
| 3d$^7$(2P)$^4p$ | $x^3D$ | 3  | 67524.021            | 3  | 10.5      | 1.5            | -19.4     | 3.5            | 29.9    |
| 3d$^7$(a$^2D$)$^4p$ | $w^3D$ | 1  | 69317.077            | 1  | 22.2      | 0.7            | -8.3      | 10.0           | 30.5    |
| 3d$^7$(2H)$^4p$ | $z^3I$ | 6  | 69617.495            | 1  | 24.0      | 2.0            | -6.7      | 3.4            | 30.7    |

$^a$ Ding & Pickering [2]

$^b$ Fu et al. [1]

Columns show - level configuration, term label, $J$ value, level energy from Ding & Pickering [2], the number of lines ($N$) used by Ding & Pickering [2] to estimate $A$ constant mean values and uncertainties, $A$ constants and uncertainties by Ding & Pickering [2] and Fu et al. [1], and the difference between $A$ constants from the two publications.
very weak predicted log gf of $-3.9$ [6], its signal-to-noise ratio of 2 in the spectra used by Ding & Pickering [2] was too low for HFS analysis.

Within the 9 spectra analysed by Fu et al. [1], the two transitions at 25453.966 cm$^{-1}$ and at 25149.948 cm$^{-1}$ were likely too noisy for meaningful hyperfine structure analysis. This would have caused cascades in error for 10 other A constants on the trees of 3d$^7$(2G)4s $a^3G_5$ and 3d$^7$(2P)4s $c^3P_2$.

5. Lack of validation of A constants using transitions involving other levels

Checking consistency between the A constants published by Fu et al. [1] further supported the conclusion that their determined A constants were erroneous for the levels 3d$^7$(2G)4s $a^3G_5$ and 3d$^7$(2P)4s $c^3P_2$.

In HFS analysis using Fourier transform spectroscopy, least-squares fitting of observed line profiles of one transition often cannot fully constrain A constant values, i.e. ambiguities or a range of A values can fit the spectral line, causing large uncertainties (see Ding & Pickering [2] and Lawler et al. [3] for example). In general, the best practice is to analyse multiple transitions involving as many energy levels as possible for constraint and validation when estimating the A constant of a single level.

Fu et al. [1] had published A constants for both levels 3d$^7$(2G)4p $y^3F_4$ and 3d$^7$(2G)4s $a^3G_5$. However, these two A constants do not reproduce the line profile of the transition between their corresponding levels. The transition between these two levels was observed and analysed in the UV spectra used by Ding & Pickering [2], see figure 2. With a high signal-to-noise ratio of 950, this transition is expected to be observed in the archival spectra analysed by Fu et al. [1]. In figure 2b, only half of the total line width was characterised by the A constants from Fu et al. [1], the highest relative intensity component was also on the wrong side. It is assumed that Fu et al. [1] did not consider this transition at 41885.65 cm$^{-1}$ during their HFS analysis, as it was not listed by table 3 nor shown in figure 1 of their paper. This fit for validation would have avoided discrepancies in 7 other A constants which were dependent on the HFS analysis of 3d$^7$(2G)4s $a^3G_5$, as indicated on its tree in figure 1.

Likewise, the discrepancies in 3d$^7$(2P)4s $c^3P_2$ and 3 other energy levels of the second largest tree in figure 1 could have been avoided if the transition between energy levels 3d$^7$(2P)4p $y^3D_2$ and 3d$^7$(2P)4s $c^3P_2$ at 38729.59 cm$^{-1}$ was validated. In the spectra analysed by Ding & Pickering [2], this transition could not be fitted using the two corresponding A constants published by Fu et al. [1], see figure 3.

6. Remaining discrepancies

Discrepancies in 5 other A constants reported by Fu et al. [1] were from their HFS analysis of energy levels 3d$^7$(2P)4p $y^5D_3$, 3d$^7$(2P)4s $a^3P_1$, and 3d$^7$(2F)4p $z^5D_1$, as shown in figure 1. The disagreements in the A constants of these 3 levels are much smaller, as they were determined by Fu et al. [1] using observed and classified transitions. Though not discussed in detail, further investigation suggested the discrepancies to have arisen from the poorer quality of spectra analysed by Fu et al. [1] compared to those analysed by Ding & Pickering [2]; results from Fu et al. [1] were likely affected by factors such as lower signal-to-noise ratios, broader Doppler line widths, poorer resolutions and possibly higher amounts of self-absorption.

7. Conclusion

Fourier transform spectroscopy offers sufficient spectral resolution for accurate atomic HFS measurements, but much care is needed during line profile fitting and analysis. For Co II, magnetic hyperfine interaction A constants for 292 energy levels were previously known, of which 264 were measured for the first time by Ding & Pickering [2] using Fourier transform spectroscopy. A recent analysis of Co II Fourier transform spectra by Fu et al. [1] published 61 A constants without crucial awareness of this existing literature at the time, 17 of which were found to be inconsistent with results from Ding & Pickering [2].
Figure 2: Hyperfine structure analysis of the transition between $3d^7(^2G)4p\, y\, ^3F_4$ and $3d^7(^2G)4s\, a\, ^3G_5$ of Co II at 41885.65 cm$^{-1}$ using $A$ constants of Ding & Pickering [2] (a) and Fu et al. [1] (b). Top - diagrams illustrating hyperfine transitions between the two levels using estimated $A$ constants (1 mK = 0.001 cm$^{-1}$), level splittings not to scale. Bottom - observation (black) and fits (red dashed) of the line in a UV spectrum analysed by Ding & Pickering [2] with a signal-to-noise ratio of 950, the red vertical lines show relative intensities and wavenumbers of component transitions indicated above on the transition diagrams.

(a) Spectral line fit using $A$ constants of Ding & Pickering [2].

(b) Spectral line fit using $A$ constants of Fu et al. [1].
Figure 3: Hyperfine structure analysis of the transition between \(^{3}d\(^{7}\)(^{4}P)4p\) \(^{3}D_{2}\) and \(^{3}d\(^{7}\)(^{2}P)4s\) \(^{3}P_{2}\) of Co II at 38729.59 cm\(^{-1}\) using \(A\) constants of Ding & Pickering [2] (a) and Fu et al. [1] (b). Top - diagrams illustrating hyperfine transitions between the two levels using estimated \(A\) constants (1 mK = 0.001 cm\(^{-1}\)), level splittings not to scale. Bottom - observation (black) and fits (red dashed) of the line in a UV spectrum analysed by Ding & Pickering [2] with a signal-to-noise ratio of 40, the red vertical lines show relative intensities and wavenumbers of component transitions indicated above on the transition diagrams.
One new $A$ constant of Co II was determined by Fu et al. [1] for the energy level $3d^64s^2 \, a^3D_4$, its value of $12.0 \pm 1.8 \, \text{mK}$ was found to agree with line profiles observed by Ding & Pickering [2].

Most discrepancies are suspected to be from the HFS analysis by Fu et al. [1] of the experimentally unclassified transitions with Ritz wavenumbers $25453.966 \, \text{cm}^{-1}$ and $25149.948 \, \text{cm}^{-1}$ for the $A$ constants of the two energy levels $3d^7(^2G)4s \, a^3G_5$ and $3d^7(^2P)4s \, c^3P_2$ respectively. This likely caused a cascade of errors in the HFS analysis that was dependent on the $A$ constants of these two levels, as the two $A$ constants were shown to be unable to reproduce observed line profiles at $41885.65 \, \text{cm}^{-1}$ and $38729.59 \, \text{cm}^{-1}$. Note that Ding & Pickering [2] used 13 and 14 lines to find the $A$ constants for $3d^7(^2G)4s \, a^3G_5$ and $3d^7(^2P)4s \, c^3P_2$ respectively. Although the spectra analysed by Fu et al. [1] were likely poorer in quality compared to those analysed by Ding & Pickering [2], all discrepancies would have been minimal, if Fu et al. [1] had analysed more transitions involving other energy levels for the 17 discrepant $A$ constants.

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