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Ab initio calculations of torsionally mediated hyperfine splittings in E states of acetaldehyde



MOLECULAR SPECTROSCOPY

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ABSTRACT

Quantum chemistry packages can be used to predict with reasonable accuracy spin-rotation hyperfine interaction constants for methanol, which contains one methyl-top internal rotor. In this work we use one of these packages to calculate components of the spin-rotation interaction tensor for acetaldehyde. We then use torsion-rotation wavefunctions obtained from a fit to the acetaldehyde torsion-rotation spectrum to calculate the expected magnitude of hyperfine splittings analogous to those observed at relatively high *J* values in the E symmetry states of methanol. We find that theory does indeed predict doublet splittings at moderate *J* values in the acetaldehyde torsion-rotation constants compared to methanol, but that the factor of three decrease in hyperfine spin-rotation constants compared to methanol puts the largest of the acetaldehyde splittings a factor of two below presently available Lamb-dip resolution.

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1. Introduction

In a recent paper, experimental Lamb-dip measurements and a theoretical spin-rotation explanation were presented for the large magnetic-hyperfine doublet splittings recently observed for certain *J* and *K* values in methanol [1]. The theoretical explanation was based on torsionally mediated spin-rotation operators, which involve only the spins of the methyl protons, and which contain, in addition to the usual nuclear spin and overall rotational operators, factors in the torsional angle α of the form $e^{\pm 2i\alpha}$. These operators cannot occur in ordinary asymmetric rotors, since such molecules do not have a torsional angle variable α . In internal-rotor molecules, these hyperfine operators have non-zero matrix elements between the two components of a degenerate torsion-rotation ^{tr}E state, which gives them the property of causing the $trsA_1$ and $trsA_2$ hyperfine states associated with a given ^{tr}E state to have rather different spin-rotation coupling tensors. It is this difference that gives rise to the 30 to 70 kHz doublet splittings in methanol. (Here and below, left superscripts tr and trs will be used to indicate torsion-rotation and torsion-rotation-(nuclear)-spin symmetry species, respectively). These torsionally mediated spin-rotation operators have only zero matrix elements within ^{*tr*}A states, or within either component of a degenerate ^{*tr*}E state.

The results for methanol [1] raise the question of whether similar large torsionally-mediated spin-rotation doublet splittings can be seen in other methyl-rotor-containing molecules. In the present work, we present theoretical estimates for CH₃CHO, which has different rotational constants (*A*, *B*, *C* are all about 0.4 times those of methanol) and different torsional constants (the ratios for *F*, *V*₃, and ρ are 0.3, 1.1, and 0.4, respectively), and for which ab initio calculations are more difficult than those for CH₃OH, because CH₃CHO has one more atom, six more electrons, and a double bond.

This paper is divided into four further sections. In the second section, we present general principles that can be used to qualitatively understand the numerical results of our splitting calculations. In the third section, we show that numerical values for the spin-rotation hyperfine tensor calculated for the simpler case of methanol using three different software packages and computational levels agree well with each other. This encourages us in the fourth section to use our lower-level computations to calculate the spin-rotation hyperfine tensor of acetaldehyde, and then to use our torsion-rotation wavefunctions to estimate the magnitude of spin-rotation hyperfine splittings (as well as the line frequencies and intensities) expected for various rotational transitions in CH₃-CHO. In the fifth section, we briefly describe the experimental measurements on acetaldehyde considered here.

2. General principles

On the basis of a greatly simplified spin-rotation Hamiltonian and very approximate torsion-rotation wavefunctions, a number of general principles emerged [1] concerning the presence or absence of observable torsionally mediated hyperfine doublets at moderate to high *J* values in asymmetric rotor molecules with one internal rotor. These principles, which are illustrated by the three examples presented in Table S-1 of the supplementary material of [1], appear to hold also for the present calculations of analogous hyperfine splittings in acetaldehyde, so we summarize them now, as a framework for discussing our numerical results.

The restriction to higher *J* values is imposed to limit consideration to torsion-rotation states where spin-spin coupling effects on the hyperfine patterns are expected to be much smaller than spinrotation effects.

The presence of hyperfine doublets caused by the torsionally modulated spin-rotation operators given in Eq. (20) of [1] is related to a competition between the asymmetric-rotor term (1/2)(B-C) $(J_x^2 - J_y^2)$ and the internal-rotation term $-2F\rho P_{\alpha}J_z$ in the torsionrotation Hamiltonian of methanol or acetaldehyde (in the notation of [1]). This competition ultimately determines the main properties of any given torsion-rotation eigenfunction. The first term tries to generate limiting-case torsion-rotation eigenfunctions that exhibit properties described by the conventional asymmetric-rotor quantum numbers J_{KaKc} . The second term tries to generate limitingcase torsion-rotation eigenfunctions that exhibit properties described by the less familiar signed-K quantum numbers in J_{-K} and J_{+K} . We can think of this competition as creating a continuum of "intermediate coupling cases" between these two limiting cases.

As pointed out in Section S-B of the supplemental material to [1], the $J_{\pm K}$ limit for eigenfunctions leads to no contribution whatever to the hyperfine splitting of a given ${}^{tr}E$ level from the spinrotation operators under consideration here, so that no transitions in this limit will show measurable hyperfine doublets. The J_{KaKc} limit appears at first in Section S-B to be more promising, since individual torsion-rotation levels can have large hyperfine splittings, but the ${}^{trs}A_1 \leftrightarrow {}^{trs}A_2$ selection rules on the overall symmetry species, together with various phase factors in the wavefunctions (i.e. factors like $(-1)^J$, $(-1)^K$, etc.), conspire to make all asymmetric-rotor-allowed transitions obey top-top or bottom-bottom selections rules in the hyperfine energy-level patterns, and thus to exhibit negligibly small splittings in observed transitions. We must thus look for large hyperfine doublets in quantum number regions lying between these two limiting cases.

Even in regions of intermediate coupling, however, the situation is not always favorable. For example, *a*-type *R* branch lines of the form $(J + 1)_{Ka \cdot Kc+1} \leftarrow J_{Ka \cdot Kc}$ will not show large doublet splittings, even when the individual levels themselves do have large hyperfine splittings, because: (i) the hyperfine splitting patterns for two adjacent *J* levels in the same *K* series (i.e., with the same *J*- K_a - K_c value) will be nearly the same, differing essentially by the ratio $(J + 1)/J \approx 1$ for J >> 1, and (ii) the hyperfine selection rules for *a*-type *R* branches are top-top and bottom-bottom. The simple model used to construct Table S-1 of [1] also strongly suggests that $\Delta K_a = \pm 1$ transitions will only show measurable doublets when the intermediate coupling cases are quite different for the same *J* region of the two different K_a stacks.

Of course, in addition to the coupling cases of the torsionrotation eigenfunctions, the other important factor in generating large doublet splittings is the magnitude of various elements of the spin-rotation coupling tensor. Elements of this tensor scale roughly as the rotational constants [2], so that the tensor elements calculated below for acetaldehyde are less than half the size of those for methanol. Measurements at significantly higher J values will thus be necessary to see splittings in acetaldehyde. Another way of looking at this is to note that the magnetic field generated by molecular rotation is proportional to the angular velocity $\boldsymbol{\omega}$ [3]. For the spin-rotation terms considered here, we are interested in $\boldsymbol{\omega}_x \approx J_x | I_{xx} \propto B J_x$ and $\boldsymbol{\omega}_y \approx J_y / I_{yy} \propto C J_y$, where I_{xx} and I_{yy} are moments of inertia along the *x* and *y* principal axes. Since large doublet splittings are observed in methanol (where $(1/2)(B + C) \approx 0.8 \text{ cm}^{-1}$) for the *J* range from 13 to 34, we expect that comparable splittings for acetaldehyde (where $(1/2)(B + C) \approx 0.3 \text{ cm}^{-1}$) will occur in the *J* range from 35 to 91. Although these *J* values are rather large, reliable measurements, assignments, energy levels, and intensity calculations have recently become available for acetaldehyde torsion-rotation transitions (without Lamb-dip information) up to *I* = 66 [4].

It is not easy to obtain quantitative algebraic predictions of exactly which line to measure when searching for large hyperfine doublets in acetaldehyde, because perturbation-theory expressions for asymmetric-rotor splittings and internal-rotation splittings are not very accurate in the intermediate coupling region, even for the highly simplified one-parameter coupling model used to illustrate various points in Table S-1 of [1]. For this reason, we use the numerical calculations for acetaldehyde in Sections 3 and 4 to estimate where hyperfine splittings might be large enough to see.

3. Spin-rotation hyperfine tensors for methanol and acetaldehyde obtained from ab initio calculations

There are two ab initio calculations in the literature [5,6] for elements of the spin-rotation hyperfine tensor in methanol. Before calculating values for acetaldehyde, we recalculated the methanol values, which are compared with the literature values in Table 1. Because of differences in phase conventions (some involving unknown positive axis directions in the quantum chemistry packages), we compare only the computational levels and the magnitudes of the tensor elements here.

The calculation in [5] was performed at the CCSD(T) level with a pVTZ basis set, using the commercial [7] quantum chemistry software package ACESII [8]. Points along the internal rotation coordinate were generated by rotating an averaged rigid C_{3v} methyl-top structure taken from Ref. [9]. The calculation in [6] was also performed at the CCSD(T) level, but with an aug-cc-pVTZ basis set, using the commercial quantum chemistry software package CFOUR [10]. Points along the internal rotation coordinate were generated by rotating an averaged ab initio C_{3v} rigid methyl-top structure. Our calculation was performed at the relatively modest MP2 level with a 6-311 + G(3df,2p) basis set, using the commercial quantum chemistry software package Gaussian09 [11]. We followed essentially the procedure outlined in [5], but instead of rotating a rigid methyl group, we used optimized structures along the internal rotation coordinate that included the calculated non- C_{3v} methyl-top geometry at each point [12]. It can be seen from the Fourier expansion coefficients for elements of the spinrotation hyperfine tensor in Table 1 that magnitudes of the large coefficients from all three calculations agree well with each other. We attribute their small disagreements to differences in computational level and in the methyl top structures used in the three calculations.

There are three main computational differences between methanol (CH₃OH) and acetaldehyde (CH₃(C=O)H), because the latter molecule contains six more electrons, one more nuclear centre, and a C=O double bond. All three of these differences act to make low-level ab initio calculations less accurate for acetaldehyde than they are for methanol. Nevertheless, Table 1 shows that our relatively modest quantum chemistry calculations of the

Table 1

Fourier expansion coefficients^a for spin-rotation hyperfine constants^b in kHz for the methyl and hydroxyl hydrogens^c in CH₃OH from three different calculations^d.

A1 ^e	C0	С3	Ea,Eb ^g	C1	C2	A1 ^e	C0	C3
H654aa	-12.964	0.078	H654aa	0.111	-0.205	H1aa	-13.373	-0.388
Ref. [5]	-12.626	0.041	Ref. [5]	-0.016	0.053	Ref. [5]	-12.877	-0.347
Ref. [6]	12.486	0.052	Ref. [6]	0.741	-0.080	Ref. [6]	13.305	-0.380
H654bb	-0.612	-0.014	H654bb	0.015	1.741	H1bb	-0.726	0.020
Ref. [5]	-0.666	-0.017	Ref. [5]	0.067	1.666	Ref. [5]	-0.741	0.018
Ref. [6]	0.579	-0.018	Ref. [6]	-0.104	-1.660	Ref. [6]	0.659	0.004
H654cc	-0.729	0.005	H654cc	-0.023	-1.697	H1cc	-2.942	-0.041
Ref. [5]	-0.755	0.001	Ref. [5]	0.010	-1.662	Ref. [5]	-2.852	-0.038
Ref. [6]	0.688	0.011	Ref. [6]	-0.065	1.673	Ref. [6]	2.935	-0.048
H654ab	0.232	0.019	H654ab	2.954	0.069	H1ab	3.827	0.028
Ref. [5]	0.166	0.049	Ref. [5]	2.947	-0.011	Ref. [5]	3.656	0.025
Ref. [6]	0.441	-0.076	Ref. [6]	-2.878	0.331	Ref. [6]	3.800	-0.040
A2 ^f		C3	Ea,Eb ^h	C1	C2	A2 ^f		C3
H654bc		0.016	H654bc	-0.021	-1.715	H1bc		-0.043
Ref. [5]		0.009	Ref. [5]	-0.017	-1.665	Ref. [5]		-0.023
Ref. [6]		0.015	Ref. [6]	0.028	1.668	Ref. [6]		-0.024
H654ac		-0.015	H654ac	-3.233	-0.116	H1ac		-0.039
Ref. [5]		-0.046	Ref. [5]	-3.072	-0.006	Ref. [5]		-0.014
Ref. [6]		0.074	Ref. [6]	3.016	-0.346	Ref. [6]		0.034

^a Only the first one or two (i.e., the largest) expansion coefficients are shown in this table.

^b The last two letters in symbols like H654aa, etc. indicate tensor components labeled by the *a,b,c* principal axes of the molecule. Off-diagonal tensor elements labeled *ab*, *bc*, or *ac* are actually the averages (1/2)(*ab+ba*), (1/2)(*bc+cb*), or (1/2)(*ac+ca*), respectively.

^c H654 and H1 indicate spin-rotation constants for the three methyl H atoms and the hydroxyl H atom, respectively.

^d Expansion coefficients in rows labeled by H654aa, etc. are from the present work. The other coefficients are taken directly from Table 6 of Ref. [5] and Table 1 of Ref. [6]. No attempt was made to make signs of the expansion coefficients agree with those of the present work, so only magnitudes should be compared.

^e Spin-rotation tensor elements of species A₁, with Fourier expansions in $C_{3n} \cos 3n\alpha$.

^f Spin-rotation tensor elements of species A_2 , with Fourier expansions in $C_{3n} \sin 3n\alpha$.

^g Spin-rotation tensor elements of species E. The E_a and E_b components of rows beginning with H654 are expanded as $C_1 \cos \alpha + C_2 \cos 2\alpha + C_4 \cos 4\alpha + C_5 \cos 5\alpha$ and $-C_1 \sin \alpha + C_2 \sin 2\alpha - C_4 \sin 4\alpha + C_5 \sin 5\alpha$, respectively, as in Eq. (19) of [5]. H654aa = 0.741 [6] in this E_a, E_b group is the only significant disagreement involving large tensor elements from the three calculations shown in this table.

^h Spin-rotation tensor elements of species E. E_a and E_b components calculated in the present work are expanded as $C_1 \sin \alpha + C_2 \sin 2\alpha + C_4 \sin 4\alpha + C_5 \sin 5\alpha$ and $C_1 \cos \alpha - C_2 \cos 2\alpha + C_4 \cos 4\alpha - C_5 \cos 5\alpha$, respectively, as in Eq. (20) of [5].

spin-rotation constants for methanol agree quite well with the higher-level calculations. Parameters obtained from fitting the rather different experimental data sets in [1] and [6] also agree well with the internally consistent ab initio values for the spin-rotation constants in Table 1 (but see footnote g there). Since the purpose of this paper is to examine the possibility of observing high-*J* hyperfine doublets in a structurally related molecule, errors as high as 30% or so in the calculated spin-rotation constants will not affect our qualitative conclusions. We thus decided to perform calculations at our relatively low MP2 level to obtain the spin-rotation constants needed to estimate the hyperfine splittings for acetaldehyde in Section 4.

Table 2 presents Fourier expansion coefficients for our calculated values (in kHz) of the spin-rotation hyperfine constants in acetaldehyde. Since these coefficients are not found elsewhere in the literature, Table 2 has more detail than Table 1, i.e., it contains all coefficients used in the Fourier expansion fits (with standard errors [13] in parentheses) and the overall standard deviation σ in kHz for each fit. The full set of coefficients is not required for our hyperfine splitting estimates in the next section; we present all of them in Table 2 for completeness. The large variations in σ from one tensor element to another arise in some cases because only elements with magnitudes above 0.1 kHz are given to eight significant figures in the Gaussian output at each point along the internal-rotation path, and in other cases because even longer Fourier expansions might be required. Numerical values for H654bb, H654cc, and H654bc in the columns labeled *Cn* for n = 1and 2 in Table 2 correspond to the quantities $A_{xx}^{(n)}$, $A_{yy}^{(n)}$, and $A_{xy}^{(n)}$, respectively in Eq. (23) and Table 5 of [1]. The H1bc and H1ac values labeled "small" in Table 2 were not subjected to least squares fitting, because they were given only to one significant digit by Gaussian. (In Table 1 we chose another option and fit the step-function-like plots of H1bc and H1ac to one-term Fourier series, to permit order-of-magnitude comparison with the more precise literature values [5,6].

Since the calculations above produce ab initio structures along the internal rotation coordinate, and since elements of the tensors for nuclear spin-spin hyperfine coupling depend only on this structure [3], we give Fourier expansion coefficients for elements of the spin-spin hyperfine coupling tensors in Table S-1 of the Supplemental Material.

4. Calculated hyperfine splittings in various torsion-rotation states of acetaldehyde

Hyperfine calculations here were carried out as described in [1], i.e., eigenvectors for the acetaldehyde torsion-rotation states were calculated using a modified version [14] of the BELGI program [15] with global fit parameters and $J_{max} = 26$ taken from [16], and then expectation values of the hyperfine operators in Eq. (22) of [1] were calculated as described in that reference. One difference here is that we not only calculated hyperfine splittings for the torsional ground state $v_t = 0$, but we also made exploratory calculations in the $v_t = 1$ and 2 states. The second difference is notational. While we generally followed the notation of [1], we deviate from it here by using, in addition to the asymmetric-rotor $J_{Ka,Kc}$ notation and the internal-rotation $J_{\pm K}$ notation, a variation of the older J_{τ} notation [17], in which our counter τ increases from 1 to 2J + 1 as the eigenvalues for given J (and given v_t) increase in energy. We added this

Table 2

Fourier expansion coefficients^a for ab initio calculated elements of the symmetry-adapted spin-rotation hyperfine tensor in kHz for the methyl and hydroxyl hydrogens^b in CH₃CHO.

Ea,Eb ^c	C1	C2	$C4\times 10^{1}$	$\text{C5}\times 10^1$	$C7\times 10^2$	$\text{C8}\times 10^2$	$\sigma \times 10^3$
H654aa H654bb H654cc H654ab	-2.668541(60) 0.4481511(98) 0.0056904(59) 1.046126(26)	0.864234(60) 0.5711596(98) -0.6150126(73) -0.902223(28)	$\begin{array}{c} -1.08354(60) \\ -0.211404(95) \\ 0.269017(63) \\ 0.55623(26) \end{array}$	0.44347(60) 0.091996(95) -0.131423(93) -0.34093(27)	-0.8347(60) -0.16789(96) 0.18017(90) 0.4585(27)	$\begin{array}{c} 0.3299(60)\\ 0.04523(96)\\ -0.07179(64)\\ -0.2548(26)\end{array}$	0.5 0.1 0.07 0.2
Ea,Eb ^d H654bc H654ac	C1 -0.1988570(78) -1.546908(19)	C2 -0.5978437(72) 1.006859(19)	$\begin{array}{c} C4 \times 10^1 \\ 0.233788(74) \\ -0.69420(22) \end{array}$	$\begin{array}{c} \text{C5}\times 10^1 \\ -0.111522(74) \\ 0.39498(22) \end{array}$	$\begin{array}{c} {\rm C7}\times 10^2 \\ {\rm 0.16445(72)} \\ {\rm -0.5217(19)} \end{array}$	$\begin{array}{c} {\rm C8} \times 10^2 \\ {\rm -0.05854(76)} \\ {\rm 0.2713(19)} \end{array}$	$\begin{matrix} \sigma \times 10^3 \\ 0.07 \\ 0.08 \end{matrix}$
A1 [°] H654aa H654bb H654cc H654ab H1aa H1bb H1cc H1ab	C0 -4.4080943(43) -0.60920230(46) -0.51296483(53) -0.33233713(57) -4.4691361(37) 1.12733677(77) -0.71453571(55) 0.3546764(23)	$\begin{array}{c} C3 \times 10^1 \\ -0.306366(60) \\ 0.0565405(56) \\ 0.0041913(92) \\ -0.4509870(64) \\ -1.006584(51) \\ -0.080874(11) \\ -0.1215039(76) \\ -0.519036(32) \end{array}$	$\begin{array}{c} {C6 \times 10^2} \\ -0.39178(60) \\ 0.050860(70) \\ 0.007482(58) \\ -0.064574(66) \\ -0.46249(51) \\ -0.07824(11) \\ -0.018540(76) \\ -0.22522(32) \end{array}$	$\begin{array}{c} C9 \times 10^3 \\ -0.5152(60) \\ 0.05137(60) \\ 0.03878(85) \\ -0.01392(77) \\ -0.4415(51) \\ -0.0750(11) \\ 0.02373(76) \\ -0.1980(32) \end{array}$	$\begin{array}{c} \sigma \times 10^3 \\ 0.05 \\ 0.005 \\ 0.005 \\ 0.004 \\ 0.04 \\ 0.009 \\ 0.007 \\ 0.03 \end{array}$		
A2 ^f H654bc H654ac H1bc H1ac		C3 × 10 ¹ -0.02669(24) 0.30515(47) Small Small			0.2 0.3		

^a The last two letters in symbols like H654aa, H1aa, etc. indicate tensor components labeled by the *a*,*b*,*c* principal axes of the molecule. Off-diagonal tensor elements labeled *ab*, *bc*, or *ac* are actually the averages (1/2)(ab+ba), etc. Numbers in parentheses are one standard uncertainty in the last two digits (type A, k = 1)[13]; σ is the overall standard deviation of the fit in kHz. Some expansion coefficients cannot be well determined because the corresponding spin-rotation hyperfine tensor components fall below a printout cut-off in Gaussian for some values of the internal rotation angle.

PH654 and H1 indicate spin-rotation constants for the three methyl H atoms and for the hydroxyl H atom, respectively.

^c Spin-rotation tensor elements of species E. The E_a and E_b components are expanded as $C_1 \cos \alpha + C_2 \cos 2\alpha + C_4 \cos 4\alpha + C_5 \cos 5\alpha$ and $-C_1 \sin \alpha + C_2 \sin 2\alpha - C_4 \sin 4\alpha + C_5 \sin 5\alpha$, respectively.

^d Spin-rotation tensor elements of species E. E_a and E_b components are expanded as $C_1 \sin \alpha + C_2 \sin 2\alpha + C_4 \sin 4\alpha + C_5 \sin 5\alpha$ and $C_1 \cos \alpha - C_2 \cos 2\alpha + C_4 \cos 4\alpha - C_5 \cos 5\alpha$, respectively.

^e Spin-rotation tensor elements of species A₁, with Fourier expansions in $C_{3n} \cos 3n\alpha$.

Spin-rotation tensor elements of species A_2 , with Fourier expansions in $C_{3n} \sin 3n\alpha$.

Table 3

Comparison of the τ and K labeling schemes for $v_t = 0$ and 1 levels^a in three works on torsion-rotation energy levels in acetaldehyde.

$\tau^{\rm b}$ $\pm K_a$ $K_c^{\rm c}$ K_a $K_c^{\rm d}$	$\tau^{\mathbf{b}} = \pm K_a$	K_c^{c} K_a	K_c^{d} τ^b	$\pm K_a \qquad K_c^{c}$	$K_a \qquad K_c^{d}$
1 0 J 0 J	6 –3	J -2 3	J – 2 11	-5 J -5	5 J –5
2 –1 J 1 J	7 +3	J – 3 3	J – 3 12	+6 J -5	6 J –5
3 +1 J-1 1 J-	1 8 -4	J – 3 4	J – 3 13	-6 J-6	6 J –6
4 –2 J–1 2 J–	1 9 +4	J – 4 4	J – 4 14	+7 J -6	7 J –6
5 +2 J -2 2 J -	2 10 +5	J -4 5	J -4 15	_7 J_7	7 J –7

^a For v_t = 2 levels, avoided crossings associated with large internal-rotation effects make the τ and *K* correspondences depend on the *J* value of the manifold (see text).

^b This work: τ increases monotonically from 1 to 2*J* + 1 as the energies of the torsion-rotation levels for given v_t and *J* increase. ^c Ref. [19]: + K_a and $-K_a$ labels are assigned according to the dominant basis-set component in any torsion-rotation eigenfunction.

The correspondences in this table are for $v_t = 0$ levels. For $v_t = 1$ levels the signs of + K_a and $-K_a$ quantum numbers must be reversed.

 K_c labels are added so that levels with $K_c = J - |K_a| + 1$ always lie below levels with $K_c = J - |K_a|$ for the same $|K_a|$.

^d Ref. [4]: K_a and K_c labels are assigned within a given v_t and J manifold using the traditional asymmetric-rotor ordering [17].

simple counting notation because energy levels for asymmetric rotors with internal rotation splittings do not always follow the normal $K_a K_c$ order [18].

Table 3 gives the correspondence for $v_t = 0$ and 1 between various τ and *K* labeling schemes used in acetaldehyde papers cited here. The correspondence for $v_t = 2$ is more complicated because of the larger internal-rotation effects and the large number of avoided crossings. The avoided crossings in fact make the τ and *K* correspondences depend on the *J* value of the manifold. For the $v_t = 2$, J = 5 manifold, for example, $\tau = 1$ to 11 in the present work correspond to (K_{a} , K_c) = (-2,4), (-1,5), (-3,3), (0,5), (1,4), (2,3), (-4,2), (3,2), (4,1), (5,1), (-5,0) in [19] and to (K_a , K_c) = (0,5), (1,5), (1.4), (2.4), (2,3), (3,3), (3,2), (4.2), (4,1), (5,1), (5,0) in [4].

For simplicity, we make three approximations in our calculations of the doublet splittings for acetaldehyde. (i) We use only the three tensor elements H654bb, H654cc, and H654bc of C2 type in Table 2. This seems reasonable for two reasons. First these three parameters proved to be the only ones needed to fit the methanol splittings in Ref. [1]. Second, the corresponding three parameters of C1 type in Table 2 are smaller than their C2 counterparts. (ii) We use tensor components given by Gaussian in the principal axis system as if they were tensor components in the rho axis system [18] used for the torsion-rotation Hamiltonian of acetaldehyde. It can be seen in Fig. 3 of [18] that these two axis systems only differ by a rotation of a few degrees about the *c* axis. (iii) As mentioned earlier, we were unable to determine with certainty the positive directions used for the principal axes in the Gaussian calculations of the hyperfine spin-rotation constants, which then makes the sign of H654bc uncertain in our axis system. Results are thus presented in this section for calculations using the "experimental positive sign" determined for H654bc in methanol [1], which is opposite to the sign of C2 for H654bc in Table 2. Exploratory calculations using the other sign (two of which are shown in the supplemental material) indicate that details of the calculated splittings change, but the qualitative conclusion that hyperfine splittings

remain just below present Lamb-dip resolution capabilities does not change.

We present our exploratory calculated results either as graphs of hyperfine splittings plotted against I < 40 for individual I levels with a given value of v_t and τ , or as graphs of the doublet splittings expected in transitions with increasing J belonging to a given $\tau' \leftarrow \tau''$ branch. The plots for individual *J* levels correspond, in the notation of [1], to graphing the level splittings in kHz shown at the bottom of Fig. 8 there. These level splittings are equal to the product of the quantities in the first two columns of Table 5 of [1], where the left-hand column contains a spin-rotation constant, and the right-hand column contains an expectation value for the operator listed. The doublet splitting for a transition between states J', τ' and J'', τ'' is equal to the sum or the difference of the splittings in the upper and lower J,τ states, depending in a somewhat complicated way on various phase factors associated with ΔI and $\Delta \tau$, as illustrated in Fig. 8 of [1]. The I < 40 cutoff in the figures below arises because we used the torsion-rotation constants of [16] in the BELGI program of [14], and extrapolations much beyond the I = 26 energy levels that were sampled [16] experimentally are known to often be unreliable. The graphs showing calculated doublet splittings for transitions also display calculated frequencies and intensities in the notation of [19] for these transitions.

4.1. Ground state calculations

Fig. 1 shows torsionally mediated hyperfine splittings of individual rotational levels from J = 10 to 40, for $\tau = 1$ and 2 in the $v_t = 0$ torsional state. For J = 15, the $\tau = 1$ and 2 levels correspond in the acetaldehyde atlas [19] to 15₀ and 15₋₁ levels in signed-*K* notation, or to the 15_{0,15} and 15_{1,15} levels in asymmetric-rotor notation. These high-*J*, low-*K*, $v_t = 0$ levels of acetaldehyde are expected to be in the asymmetric-rotor limit, where relatively large spin-rotation hyperfine splittings occur in each individual state (as implied by Table S-1 of [1]). The nearly linear increase in splitting with *J* supports this expectation. The linear increase can also be used to estimate that *J* values greater than 57 will be necessary to achieve splittings in individual rotational states of acetaldehyde that are larger than 30 kHz.

Fig. 2 shows transition frequencies, hyperfine splittings, and intensities for the $\tau = 2 \leftarrow 1$ Q-branch and R-branch lines arising from the energy levels in Fig. 1. These transitions correspond to $K = -1 \leftarrow 0$ in signed K notation and to the $K_a = 1 \leftarrow 0$ c-type Q branch and *b*-type R branch in asymmetric-rotor notation. As expected from the general principles [1] summarized in Section 2, the *c*-type Q branch is strongly forbidden in acetaldehyde in the asymmetric-rotor limit. (The fact that we are in this limit at higher



Fig. 1. Torsionally mediated hyperfine splittings of individual rotational levels with $10 \le J \le 40$ and $\tau = 1$ (**O**) and 2 (×) in the $v_t = 0$ torsional state of CH₃CHO.



Fig. 2. Transition frequencies (**m**), intensities (**A**), and torsionally mediated doublet splittings (•) for the $\tau = 2 \leftarrow 1$ Q branch and R branch in the $v_t = 0$ torsional state of acetaldehyde. (J" is the lower-state J value). Doublet splittings are shown in kHz on the left vertical axis in black. Transition frequencies are shown in GHz on the right vertical axis in red. Intensities are calculated in the same units as [19]; they are given by the numbers on the left axis for the R branch and by the left-axis numbers $\times 10^{-5}$ for the Q branch. Most of the R-branch lines from J" = 0 to 65 are observed in [4]; Q-branch lines are observed there only for J = 1 and 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

J is confirmed by the decrease in transition frequency of these Q-branch lines as *J* increases and K_c clustering becomes more pronounced). Spin-rotation hyperfine splittings in this Q branch (which are essentially the sum of the individual level splittings in Fig. 1) approach 40 kHz at J = 40. The asymmetric-rotor-allowed *b*-type R branch has just the opposite behavior, i.e., good intensity, but negligible hyperfine splittings (since these are essentially the difference of the individual level splittings in Fig. 1). We thus conclude that neither of these branches is a good candidate for observing large hyperfine doublets (except perhaps in the J = 15 to 20 range of the Q branch, using a high-resolution room-temperature spectrometer operating below 20 GHz).

We now turn to another example calculation, involving E levels with |K| values of 4 and 5. These *K* values were chosen in the hope that the competition between asymmetric-rotor splittings, which initially increase with *J* approximately as $[(C-B)/(2A-B-C)]^{K}J^{2K}/{8^{K-1}[(K-1)!]^2}$ for J >> K [17], and internal-rotor splittings, which increase with *K* approximately as $-2F\rho\langle P_{\alpha}\rangle K$, will be different enough for the upper and lower states of transitions in *J* regions of measurement interest to cause large hyperfine doublets. Fig. 3 is analogous to Fig. 1, and shows the hyperfine splittings of individual *J* levels from 10 to 40 for the $\tau = 8$, 9, 10, and 11 states (i.e., for the signed $K = \pm 4$ and ± 5 states in [19], respectively). Fig. 3 shows that these individual states have very small hyperfine splittings until about J = 18 (for |K| = 4 levels) and J = 23 (for |K| = 5 levels), as expected for the internal-rotor-coupling limit. It is also obvious from Fig. 3 that all hyperfine splittings in transitions between K = 4



Fig. 3. Torsionally mediated hyperfine splittings of individual rotational levels from J = 10 to 40, for $\tau = 8$ to 11 ($K = \pm 4$ and ± 5 [19]) in the $v_t = 0$ torsional state. Note the very small splittings in the nearly pure internal-rotor coupling case at low *J*.



Fig. 4. Transition frequencies (\blacksquare), intensities (\blacktriangle), and torsionally mediated doublet splittings (•) for the $\tau = 10 \leftarrow 8$ Q branch and P branch in the $v_t = 0$ torsional state of acetaldehyde. (J' is the $\tau = 8$ J value.) Doublet splittings are shown in kHz on the left vertical axis in black. Transition frequencies are shown in GHz on the right vertical axis in red. Intensities are calculated in the same units as [19], and are given on the left axis. Q-branch lines are observed in [4] from J = 16 to 59; P-branch lines are observed there only for $J' = J(\tau = 8)$ from 16 to 19 and (as R-branch lines) for J ($\tau = 10$) from 24 to 28.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and 5 levels with *J* < 40 will be below about 25 kHz, and thus below present Lamb-dip measurement capabilities.

It is still of interest to look at Figs. 4 and 5 in some detail, however, since they represent concrete examples of the general relations between *J* values, intensities, and hyperfine splittings for Q and P branch transitions involving these *K* values. Such information will be useful when trying to extend the measurements or cal-



Fig. 5. Transition frequencies (\blacksquare), intensities (\blacktriangle), and torsionally mediated doublet splittings (•) for the $\tau = 11 \leftarrow 9$ Q branch and P branch in the $v_t = 0$ torsional state of acetaldehyde. (J'' is the $\tau = 9$ J value.) Doublet splittings are shown in kHz on the left vertical axis in black. Transition frequencies are shown in GHz on the right vertical axis in red. Intensities in the units of [19] are given on the left axis. Many of the Q branch lines in Fig. 5 are observed in [4] in the range from J = 17 to 52; P branch lines are observed there only for J'' = 9 ($\tau = 9$) from 16 to 19 and (as R branches) for J ($\tau = 11$) from 23 to 27. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

culations to higher *J* values, where hyperfine splittings might be larger.

Fig. 4 shows doublet splittings, intensities, and transition frequencies for the $\tau = 10 \leftarrow 8$ Q-branch, which at low *J* can be thought of as a forbidden $K = +5 \leftarrow -4$ transition. This branch thus has negligible intensity for $J \leq 16$, as can be seen from the green triangles. At high *J*, the branch can be thought of as an asymmetric-rotor *b*-type Q branch, which is allowed with strong intensity, as can be seen from the green triangles for $J \geq 25$. As expected from the general principles in Section 2, terms in the torsionally induced spin-rotation coupling mechanism considered here give extremely small doublet-splitting contributions to these Q-branch lines in the $J \leq 16$ internal-rotor limit, but the lines do begin to show splittings of a few kHz around J = 40.

Fig. 4 also shows the $\tau = 10 \leftarrow 8$ P-branch, which at low *J* can again be thought of as a forbidden $K = +5 \leftarrow -4$ transition, and at high *J* as a forbidden asymmetric-rotor *c*-type P branch. Such a transition has vanishing intensity at both low *J* and high *J*, but gains a little intensity in the intermediate coupling region (i.e., at intermediate *J*). This c-type P branch might be expected to exhibit measurable hyperfine splittings, but in fact it does not do so up to J = 40, and the low intensities above J = 40 are expected to make transitions too weak to permit Lamb-dip measurements.

Fig. 5 shows doublet splittings, intensities, and transition frequencies for the $\tau = 11 \leftarrow 9$ Q branch, which corresponds to the forbidden $K = -5 \leftarrow +4$ transition at low *J*, and changes to an asymmetric-rotor allowed *b*-type Q branch at high *J*. The doublet-splitting and intensity behavior in this Q branch thus resembles that of the Q branch in Fig. 4. Similarly, the P branch in Fig. 5, which is similar to the P branch in Fig. 4, has no intensity in the low-*J* and high-*J* limits, and very little intensity in the intermediate *J* region, but in contrast to Fig. 4, this *c*-type P branch does have reasonably large hyperfine splittings, of about 15 kHz at J = 40 (and possibly much larger at J = 60).

Figs. S-1 to S-4 in the supplementary material are similar to Figs. 4 and 5, except that the Q branches are *c*-type and the P branches are *b*-type. The *b*-type P branch in Fig. S-4 has hyperfine splittings of about 8 kHz at J = 40, but the splittings are still increasing with J at that point. Since the intensities of these *b*type lines are expected to continue to increase, while their splittings will initially increase and then decrease, higher J calculations would be interesting, particularly since this P branch was observed (as an R branch in the THz region) up to $J''(\tau = 10) = 59$ in [4].

Fig. S-5 displays a $\tau = 4 \leftarrow 7$ R branch, which, because of the negative frequencies involved, is in fact a $\tau = 7 \leftarrow 4$ P branch at both low *J* and high *J*. This branch corresponds, in the notation of [19], to a forbidden $K = + 3 \leftarrow -2$ P branch at low *J*, and changes to a $\Delta K_a = 1$, $\Delta K_c = 3$ *b*-type R branch at intermediate *J*, and eventually to a $\Delta K_a = 1$, $\Delta K_c = 3$ *b*-type P branch at high *J*. In spite of the relatively low calculated intensities for this branch, most of the transitions (apart from a few at low frequency) are reported in [4] from $J(\tau = 7) = 6$ to 46. Fig. S-5 suggests that the calculated doublet splittings will reach a maximum of about 20 kHz near *J* = 40, which is still a factor of two smaller than present Lamb-dip resolution [20].

4.2. First and second excited torsional state calculations

Because the $v_t = 1$ state of acetaldehyde has a torsional splitting of 1.7 cm⁻¹, which is approaching the 9 cm⁻¹ splitting of methanol, it was hoped that transitions could be found with hyperfine doublet splittings in the observable range of Lamb-dip spectroscopy. However, the splittings for individual rotational levels of $v_t = 1$ are very similar to those for $v_t = 0$ shown in Figs. 1 and 3. The relations between doublet splittings and intensities of torsion-rotation transitions are very similar to those for $v_t = 0$ shown in Figs. 2, 4 and 5, and again show that moderate hyperfine doublet splittings occur for transitions with nearly zero intensity, whereas transitions with good intensity have hyperfine splittings of a few kHz or less.

Table 4 presents values of hyperfine splittings for individual levels in acetaldehyde having the quantum numbers: $v_t = 0$, 1, 2, J = 19, 20, 21, and $\tau = 1-7$, as well as similar $v_t = 0$ splittings for methanol [1] for comparison. The largest splittings in the acetaldehyde levels are all significantly smaller than the largest methanol splittings, and the sum of acetaldehyde splittings from two different τ columns (the maximum attainable doublet splitting in a transition) never reaches 20 kHz. For this reason, we do not discuss the $v_t = 1$ and 2 acetaldehyde splittings further in this paper.

4.3. Comparison with experiment

Results of our exploratory calculations above are consistent with the six E-species acetaldehyde lines examined recently (see Section 5) using Lamb-dip spectroscopy [20]. Table 5 shows that the doublet splittings calculated for these lines are all a few kHz or less, in good agreement with the fact that no evidence of splittings or broadenings was observed experimentally.

5. Lamb-dip measurements

While the theoretical work described above was going on, a number of Lamb-dip measurements on acetaldehyde and methylamine [20] were performed in Kharkiv at frequencies from 50 to 150 GHz. As noted above, none of the lines examined showed any evidence of anomalous hyperfine splittings or unusual broadening.

The main problem during the experimental investigation was to avoid possible distortion of the line shape caused by modulation effects, because small splittings may also manifest themselves as a relatively small change in the shape of the spectral line (or Lamb dip). For this reason, we must be sure, when trying to detect such splittings, that distortions dealing with modulation effects are negligible. In order to solve this problem we performed a series of spectral recordings in which both the depth and frequency of modulation were decreased. Naturally, the lower the parameters used for frequency modulation are, the poorer the signal-to-noise ratio for a single scan becomes. To obtain acceptable signal-to-noise

Table 4

 $Calculated \ Hyperfine \ Splittings^a \ in \ kHz \ for \ Individual \ E \ Levels \ of \ Acetaldehyde \ with \ Quantum \ Numbers \ 0 \leq \nu_t \leq 2, \ 19 \leq J \leq 21, \ and \ 1 \leq \tau \leq 7.$

$CH_3CHO v_t =$	0						
J	τ = 1	2	3	4	5	6	7
21	8.557	8.950	0.297	2.840	4.999	0.152	3.121
20	7.928	8.407	0.796	2.523	4.799	0.167	2.616
19	7.294	7.873	1.232	2.229	4.546	0.164	2.147
$CH_3CHO v_t =$	1						
J	τ = 1	2	3	4	5	6	7
21	6.531	6.760	1.731	0.401	5.651	0.736	2.923
20	6.000	6.267	2.132	0.091	5.511	0.526	2.311
19	5.469	5.778	2.482	-0.173	5.308	0.348	1.778
$CH_3CHO v_t =$	2						
J	$\tau = 1$	2	3	4	5	6	7
21	6.547	8.835	-0.114	7.349	0.848	2.659	0.148
20	5.946	8.408	0.277	7.010	0.903	2.371	0.219
19	5.371	7.988	0.607	6.593	0.953	1.934	0.176
$CH_3OH v_t = 0$	b						
J	$\tau = 1$	2	3	4	5	6	7
	K = -1	0	+ 1	+ 2	-2	+ 3	-3
21	34.176	18.007	1.274	3.474	21.572	0.031	0.716
20	32.723	16.307	1.196	3.049	19.450	0.029	0.563
19	31.246	14.630	1.116	2.565	17.290	0.025	0.438

^a These acetaldehyde splittings were calculated with H654bb = 0.58077, H654cc = -0.61570, and H654bc = +0.59620 from an early fit, i.e., the sign of H654bc has been changed from that in Table 2 to agree with the experimental sign determined for this quantity in methanol [1].

^b The last six rows contain the analogous $v_t = 0$ calculations for methanol, taken from Fig. 8 of [1].

Table 5
Comparison of theory and experiment for six lines of E species in acetaldehyde.

Frequency ^a	Transition ^b					Hyperfine Splitting ^c		Transition ^d				Branch type		
	vt	J	τ'	\leftarrow	<i>J</i> ″	τ"	Calc	Obs	K_{a}'	K_c'	~	K_a''	<i>K</i> _c "	
105813.016	0	25	14	\leftarrow	26	12	0.01	None	+ 7	19	\leftarrow	+ 6	21	c-type P
105963.809	0	25	15	\leftarrow	26	13	0.02	None	-7	18	\leftarrow	-6	20	c-type P
110903.606	0	23	6	\leftarrow	22	9	1.1	None	-3	21	\leftarrow	+4	18	b-type R
111757.493	0	32	10	\leftarrow	31	12	2.0	None	+ 5	28	\leftarrow	+ 6	26	c-type R
108307.408	1	12	3	\leftarrow	12	1	5.6	None	-1	11	\leftarrow	0	12	b-type Q
108521.908	1	17	5	\leftarrow	16	7	5.4	None	-2	15	\leftarrow	-3	13	c-type R

^a Torsion-rotation transition frequency in MHz [4].

^b Upper-state J and τ quantum numbers on the left, lower-state on the right. For the numerical counter τ see text; v_t is the harmonic-oscillator-like quantum number of the torsional vibration.

^c Doublet splitting in kHz for the transition in each row. For calculated and observed values, see Sections 4 and 5, respectively; "none" means no splitting or broadening was detected at the approximately 30 kHz linewidths of the Lamb-dip measurements.

^d Upper-state asymmetric-rotor quantum numbers on the left, lower-state on the right, in the notation of Ref. [19].



Fig. 6. Lamb-dip record of the $23_{-3,21} \leftarrow 22_{4,18}$ line of acetaldehyde in Table 5. The dotted line is the initial experimental record (1f detection). The thin solid line is the experimental record after subtraction of the simulated Doppler profile (dot-dash line). The thick solid line is a one-line Lorentz approximation of the observed Lamb dip, which is in very good agreement with the observed shape of the Lamb dip. The inset in the upper-left corner shows a numerical second-derivative of the experimental record, to facilitate comparison with lines from instruments using 2f detection.

ratios we therefore carried out multi-scan averaging (of up to several thousand scans).

A Lamb-dip recording of one of the transitions in Table 5, obtained with a frequency modulation of 1.5 kHz and a modulation depth of 4 kHz, is shown in Fig. 6. The dotted line in Fig. 6 is the initial experimental record, the dot-dash line is the simulated Doppler line shape, the thin solid line is the experimental record after subtraction of the Doppler profile, and the thick solid line is a Lorentz approximation of the observed Lamb dip. It is evident that this one-line Lorentz approximation is in good agreement with the observed shape of the Lamb dip.

To reach the best accuracy we used first harmonic detection [21]. It should be mentioned, however, that second harmonic detection is very popular in many spectroscopic laboratories (recorded lines are in the form of the second derivative). Thus, to permit comparison of our results with measurements performed in other laboratories, we placed an insert in Fig. 6 showing the numerical second derivative of the Lamb dip obtained directly from the initial record. The experimental width of this second derivative Lamb dip is about 15 kHz.

6. Concluding remarks

The present study used a Gaussian quantum chemistry package for the calculation of spin-rotation hyperfine interaction constants for acetaldehyde. The Fourier coefficients of three of these, H654bb, H654cc and H654bc, were combined with torsionrotation wavefunctions obtained from a fit to the acetaldehyde torsion-rotation spectrum to calculate the magnitude of hyperfine doublet splittings analogous to those observed at relatively high I values in the E symmetry states of methanol. While the calculated doublet splittings are all small and below current Lamb-dip resolution, three main conclusions resulting from our calculations are summarized here. (i) Comparison of three levels of quantum chemistry calculations of the spin-rotation hyperfine interaction constants for methanol shows that reasonable accuracy and good agreement exists between MP2/6-311 + G(3df,2p) results and higher-level CCSD(T)/pVTZ and CCSD(T)/aug-cc-pVTZ results. (ii) Results for acetaldehyde are in agreement with the principles illustrated for methanol in Table S-1 of [1], namely transitions with high intensity generally have very small doublet splittings, while transitions with large doublet splittings generally have very low intensity. (iii) Our small calculated doublet splittings for six E lines in acetaldehyde agree well with the absence of observed splittings or broadenings in Lamb-dip traces for these lines.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jms.2017.06.008.

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