

The anharmonic force field of ethylene, C₂H₄, by means of accurate *ab initio* calculations

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(Received 21 February 1995; accepted 9 May 1995)

The quartic force field of ethylene, C₂H₄, has been calculated *ab initio* using augmented coupled cluster, CCSD(T), methods and correlation consistent basis sets of *spdf* quality. For the ¹²C isotopomers C₂H₄, C₂H₃D, H₂CCD₂, *cis*-C₂H₂D₂, *trans*-C₂H₂D₂, C₂HD₃, and C₂D₄, all fundamentals are reproduced to better than 10 cm⁻¹, except for three cases where the error is 11 cm⁻¹. Our calculated harmonic frequencies suggest a thorough revision of the accepted experimentally derived values. Our computed and empirically corrected *r_e* geometry differs substantially from experimentally derived values: Both the predicted *r_z* geometry and the ground-state rotational constants are, however, in excellent agreement with experiment, suggesting revision of the older values. Anharmonicity constants agree well with experiment for stretches, but differ substantially for stretch–bend interaction constants, due to equality constraints in the experimental analysis that do not hold. Improved criteria for detecting Fermi and Coriolis resonances are proposed and found to work well, contrary to the established method based on harmonic frequency differences that fails to detect several important resonances for C₂H₄ and its isotopomers. Surprisingly good results are obtained with a small *spd* basis at the CCSD(T) level. The well-documented strong basis set effect on the *ν*₈ out-of-plane motion is present to a much lesser extent when correlation-optimized polarization functions are used. Complete sets of anharmonic, rovibrational coupling, and centrifugal distortion constants for the isotopomers are available as supplementary material to the paper via the World-Wide Web. © 1995 American Institute of Physics.

I. INTRODUCTION

Any accurate *ab initio* calculation has two main issues to contend with: convergence in the one-particle space (i.e., the finite basis set) and truncation of the *n*-particle space (the electron correlation method). The development of efficient and accurate electron correlation methods such as CCSD(T) (i.e., coupled cluster¹ theory with all single and double substitutions^{2,3} with a quasiperturbative account for triple excitations⁴) has more or less resolved the *n*-particle space convergence issue for molecules that do not exhibit pathological nondynamical correlation effects.^{5,6} Advances in algorithms, software, and computer technology, on the other hand, have made it possible to routinely use one-particle basis sets of *spdf* and even *spdfg* quality. This has finally turned chemical accuracy calculations into reality, rather than a publicity slogan. For example, in a recent systematic study,⁷ total atomization energies could be predicted to within as little as 0.5 kcal/mol mean absolute error, and geometries to within as little as 0.001 Å using simple empirical corrections.

Recently, the authors have been involved in a series of papers^{8–22} in which anharmonic force fields of small polyatomics were calculated using the CCSD(T) method with

basis sets of *spdf* and *spdfg* quality. Not nearly all problems have been resolved—for example, one-particle basis set deficiencies still show up in the lowest bending frequency of C₂H₂²¹—but on the whole, reproduction of fundamentals to better than 10 cm⁻¹ is the norm.

While the technique has become essentially routine for triatomic molecules, and there have been several successful applications to tetratomics (e.g., C₂H₂,²¹ H₂CO,¹² and H₂CS²⁰), the largest molecule treated so far has been CH₄,¹⁵ which is a highly symmetric penta-atomic molecule. CH₄ is also the largest molecule for which reasonably accurate experimental anharmonic force field information is available.^{23,24}

An obvious candidate for the next step would be the ethylene molecule, C₂H₄. While it has been the subject of considerable experimental studies (e.g., an extensive series of papers by Duncan and co-workers^{25–35}), the size of the molecule (12 vibrational degrees of freedom) precluded any comprehensive experimental analysis, although a generalized harmonic force field (GHFF) has been derived^{27,29} and the Fermi resonance polyads in various isotopomers have been analyzed using local mode models.^{30–32,34,35} As a result, val-

ues are known for almost all fundamentals of the following ¹²C isotopomers: C₂H₄, C₂H₃D, H₂CCD₂, *cis*-C₂H₂D₂, *trans*-C₂H₂D₂, C₂HD₃, and C₂D₄, as well as for some ¹³C species, and full sets of accurate fundamentals are available for C₂H₄^{36–41} and for H₂CCD₂.^{42–44} From the GHFF, estimated harmonic frequencies are available,²⁷ using new and more experimental data, this analysis was later refined.²⁹

Less information is available on the geometry. *r*₀ geometries have been derived by Allen and Plyler,⁴⁵ as well as by Duncan *et al.*²⁵ An *r*_g geometry was obtained from electron diffraction data by Kuchitsu,⁴⁶ who also derived an *r*_z geometry and a “crude guess” of the actual equilibrium geometry *r*_e. More precise *r*_z geometries were obtained by Duncan²⁸ and by Hirota *et al.*⁴⁷ No accurate *r*_e geometry has been obtained to date. (A concise discussion of the relationship between the various kinds of measured geometries has been given by Kuchitsu.⁴⁸) Accurate rotational constants up to sextic centrifugal distortion have, however, been published by Cauuet *et al.*,³⁸ who also analyzed the Coriolis interaction polyad involving {*ν*₄, *ν*₇, *ν*₁₀, *ν*₁₂} in detail. Coriolis interaction is of greater than apparent interest for ethylene, since virtually the only way to study *ν*₄—which is both IR and Raman inactive—in detail is through its Coriolis interaction with the other modes (see, e.g., Refs. 38 and 39).

Among the first correlated *ab initio* studies of C₂H₄ was the work of Lee *et al.*,⁴⁹ who performed SCF, TCSCF (two-configuration SCF), CISD (configuration interaction with all single and double excitations), and 2RCISD (two-reference CISD) calculations with double-zeta plus polarization (DZP) and triple-zeta plus two polarization (TZ2P) basis sets. (While C₂H₄ is not usually thought of as a multireference system, the $\pi^2 \rightarrow \pi^{*2}$ excitation is quite important and has a coefficient of -0.213 in the 2RCISD/DZP calculation at the computed equilibrium geometry.) TCSCF is seen to result in a marked improvement over SCF, while CISD and 2RCISD are of comparable quality for this molecule. Perhaps the most noteworthy feature is the severe basis set dependence of the asymmetric out-of-plane frequency ω_8 , which increases from 816 to 939 cm⁻¹ upon improving the level of theory from 2RCISD/DZP to 2RCISD/TZ2P. (The experimental fundamental²⁷ is 940 cm⁻¹.)

Clabo *et al.*⁵⁰ computed the quartic force field at the SCF/DZP level, and combined the resulting anharmonicities with CISD/DZP harmonic frequencies. As to be expected at this level of theory, agreement between computed and experimental harmonics and fundamentals left something to be desired. From experimental rotational constants²⁶ and computed rovibrational coupling constants,⁵⁰ an estimated *r*_e geometry was derived that is “broadly consistent” with Kuchitsu’s.⁴⁶

Handy and co-workers⁵¹ obtained harmonic frequencies at the MP2 (second order Møller–Plesset perturbation theory⁵²) level⁵³ with large basis sets (up to *spdf* quality) as well as using Becke–Lee–Yang–Parr⁵⁴ (BLYP) density functional theory. Among lower-level calculations, we mention the MP2/6-31G* study by Pople *et al.*⁵⁵ as well as an MP2/6-31G scaled quantum mechanical (SQM)⁵⁶ force field study.⁵⁷

To date, no really accurate anharmonic force field of

ethylene has been provided, although Machida and Tanaka⁵⁸ have presented a GHFF supplemented with a few anharmonic force constants. The purpose of the present paper is an attempt to remedy this situation.

II. COMPUTATIONAL METHODS

All calculations were performed at the CCSD(T)⁴ level of electron correlation. The acronym stands for CCSD (coupled cluster with all single and double substitutions)^{2,3} augmented with a quasiperturbative account for connected triple excitations.⁴ Extensive applications^{7,59} have shown this method to consistently yield results very close to full configuration interaction if nondynamical correlation effects are not too large, that is, if the \mathcal{S}_1 diagnostic⁶⁰ is not too high. [For ethylene, $\mathcal{S}_1=0.011$ only, which indicates a system largely dominated by a single reference configuration. This is further supported by the coupled-cluster amplitude (intermediate normalization) for the $\pi^2 \rightarrow \pi^{*2}$ excitation, which is -0.12 .]

Two basis sets, all of the correlation consistent⁶¹ family of Dunning and co-workers, have been considered. These are denoted cc-pVnZ, i.e., correlation consistent polarized valence *n*-tuple zeta, where *n*=*D* for double and *T* for triple zeta. The cc-pVDZ and cc-pVTZ basis sets correspond to [3*s*2*p*1*d*/2*s*1*p*] and [4*s*3*p*2*d*1*f*/3*s*2*p*1*d*] contractions of (9*s*4*p*1*d*/4*s*1*p*) and (10*s*5*p*2*d*1*f*/5*s*2*p*1*d*) primitive sets where, as customary, the part after the slash denotes the basis set for hydrogen. For ethylene, these basis sets involve 48 and 116 basis functions, respectively. The carbon (1*s*)-like orbitals were constrained to be doubly occupied in the calculation, and spherical harmonics rather than Cartesian *d*,*f* functions were employed throughout.

To facilitate comparisons, the symmetry coordinates were defined exactly as in the work of Lee *et al.*⁴⁹ The geometry was first optimized to six figures or better using repeated multivariate parabolic interpolation, where the step size was reduced progressively as convergence was approached. A grid was then set up of all the points required to determine all nonvanishing quadratic, cubic, and quartic force constants by central finite differences. Cartesian coordinates were determined for all these points, and the symmetry-unique geometries identified by comparing sorted distance matrices. Thus a “petite list” of 838 points remained, of which 129 have *D*_{2*h*} symmetry, 402 and 279 belong to subgroups of order four and two, respectively, and 28 have no symmetry at all. After the energies are obtained for each point, they are mapped to the “grande list” by reversing the algorithm, and the force field in symmetry-adapted internal coordinates is obtained.

The individual energy calculations involved in mapping the potential energy surface were run on two IBM RS/6000 model 365 workstations at Limburgs Universitair Centrum (LUC) using the closed-shell coupled cluster program from TITAN⁶² interfaced to MOLCAS 2.⁶³ Together, these calculations took several months to run. Even so, a few points with point group *C*₁ (no symmetry) in the cc-pVTZ basis set could not be completed due to disk space limitations (only 2 GB of scratch space was available on each machine). These were completed on the Cray C90 at San Diego Supercom-

TABLE I. Harmonic frequencies (cm⁻¹) for C₂H₄.

		CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	Expt. Ref. 27	Expt. Ref. 29	MP2/TZ2Pf Ref. 53	BLYP/ TZ2Pf Ref. 50	CISD/ DZP Ref. 50	2RCISD/ DZP Ref. 49	2RCISD/ TZ2P Ref. 49
ω_1	A_g symm. CH stretch	3163	3157	3153	3156.2	3204	3065	3252	3246	3231
ω_2	A_g CC stretch	1671	1672	1655	1656.4	1691	1635	1737	1699	1709
ω_3	A_g symm. HCH bend	1358	1369	1370	1372.3	1390	1348	1410	1387	1398
ω_4	A_u H ₂ C-CH ₂ twist	1030	1047	1044	1044.6	1078	1036	1070	1041	1061
ω_5	B_{1g} <i>trans</i> CH stretch	3233	3219	3232	3206.9	3280	3121	3321	3318	3300
ω_6	B_{1g} anti. HCH wag	1229	1242	1245	1248.5	1251	1217	1273	1267	1277
ω_7	B_{1u} symm. out of plane	949	967	969	968.3	984	950	983	940	974
ω_8	B_{2g} anti. out of plane	909	942	959	960.3	946	948	885	816	939
ω_9	B_{2u} <i>cis</i> CH stretch	3259	3246	3234	3239.1	3304	3146	3349	3346	3321
ω_{10}	B_{2u} symm. HCH wag	820	823	843	844.1	832	818	842	837	853
ω_{11}	B_{3u} anti. CH stretch	3144	3139	3147	3129.8	3189	3054	3226	3222	3212
ω_{12}	B_{3u} anti. HCH bend	1461	1479	1473	1471.8	1487	1445	1518	1514	1524

puter Center (SDSC) using a program system composed of the two-electron integral program SEWARD⁶⁴ from MOLCAS 2, the SCF and integral transformation portions of MOLECULE-SWEDEN,⁶⁵ and the aforementioned coupled cluster program.

Finally, the spectroscopic analysis was carried out using straight second order rovibrational perturbation theory^{66,67} as implemented in the SPECTRO program.⁶⁸ Fermi resonances are treated in the customary way by deleting the resonance interaction from the contact transformation and treating it separately by diagonalizing the corresponding eigenvalue problem. Because of the number of degrees of freedom in the system (12 vibrational and 3 rotational), a variational treatment—which is definitely preferable under such circumstances—is simply not an option at present.

III. RESULTS AND DISCUSSION

Computed harmonic frequencies at the CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ levels are given in Table I,

together with previously computed values and the experimentally derived (GHFF) harmonic frequencies of Duncan *et al.*^{27,29}

Three of the CCSD(T)/cc-pVTZ harmonic frequencies, namely, ω_2 , ω_8 , and ω_{10} have errors with respect to experiment²⁷ that are definitely out of the ordinary: +17, -17, and -20 cm⁻¹, respectively. Two others, ω_5 and ω_9 , differ from the harmonic values by more than 10 cm⁻¹. The same is true with respect to the newer experimentally derived values by Duncan and Hamilton.²⁹

If we, however, compare the fundamentals (Table II), we see that most of the disagreement disappears. Here, errors for all twelve modes are below 10 cm⁻¹, with the exception of ν_8 (-10.5 cm⁻¹), for which the large basis set effect was observed in the past. It should be noted that a nonsensical value is obtained for ν_{11} unless the well known (e.g., Ref. 27) very strong Fermi type 2 resonance with $\nu_2 + \nu_{12}$ is taken into account. A milder, but still important, type 1 resonance $2\nu_{10} \approx \nu_2$ is seen; accounting for it changes ν_2 from 1633.7 cm⁻¹, or 8.3 cm⁻¹ too high, to 1621.3 cm⁻¹, or 4.1 cm⁻¹ too

TABLE II. Computed and experimental fundamentals for C₂H₄.

	CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	Expt. Ref. 26	CISD/ DZP ^a Ref. 50	2RCISD/ DZP ^a Ref. 49	2RCISD/ TZ2P ^a Ref. 49
ν_1	3015.7	3016.0	3022.03 ³⁶	3129	3123	3108
ν_2	1615.5 ^b	1621.3 ^b	1625.4 ³⁷	1703	1666	1676
ν_3	1328.9	1340.8	1343.54 ³⁶	1388	1365	1376
ν_4	1004.0	1026.2	1025.59 ³⁸	1049	1020	1040
ν_5	3084.0	3076.3	3083.36 ³⁶	3197	3193	3175
ν_6	1205.4	1223.2	1222 ³⁹	1253	1247	1257
ν_7	930.8	948.9	948.77 ³⁸	968	925	959
ν_8	892.8	929.4	939.86 ⁴⁰	868	799	922
ν_9	3106.9	3100.0	3104.89 ⁴¹	3218	3215	3190
ν_{10}	813.6	821.7	825.93 ⁴¹	841	837	853
ν_{11}	2973.6 ^c	2979.1 ^c	2988.64 ⁴¹	3085	3081	3071
ν_{12}	1420.8	1439.7	1442.47 ³⁸	1486	1482	1492

^aUsing SCF/DZP anharmonic corrections.

^bUncorrected: 1630.4 and 1633.7 cm⁻¹. Deperturbed: 1624.850 and 1626.935 cm⁻¹; $k_{2,10,10}$ =26.382 and 26.526 cm⁻¹.

^cDeperturbed: 2999.826 and 3000.712 cm⁻¹; $k_{2,11,12}$ =125.415 and 125.752 cm⁻¹.

low. While the agreement with experiment for ν_2 is not significantly enough affected to warrant inclusion, $2\nu_{10}$ changes from 1645.8 to 1658.2 cm⁻¹, in rather more pleasing agreement with the experimental value³² of 1662.2 cm⁻¹. Inclusion of a weak perturbation of ν_5 by $\nu_2 + \nu_6$ shifts ν_5 up by 1.5 cm⁻¹, but somewhat worsens agreement for ν_{11} due to the effect on deperturbed bands involving ν_2 . No evidence is seen for a perturbation $\nu_3 + \nu_2 \approx \nu_1$, which was suggested by Duncan and Hamilton²⁹ but not considered in later work.

It is not surprising, given the prominence of resonances in this molecule, that a fairly simplistic GHFF analysis results in serious errors in the harmonic frequencies. With due caution, we would suggest that our computed CCSD(T)/cc-pVTZ harmonic frequencies are more reliable than the experimentally derived ones.

The four harmonic frequencies derived by Duncan *et al.*³¹ for the CH stretching manifold from a local mode model— $\omega_1=3131.8$, $\omega_5=3200.9$, $\omega_9=3221.0$, and $\omega_{11}=3108.2$ cm⁻¹—are all systematically too low, as is to be expected since no anharmonic contributions from any of the other modes have been considered.

Returning to the harmonic frequencies (Table I), the CCSD(T)/cc-pVDZ values are surprisingly close to the CCSD(T)/cc-pVTZ ones, with the notable exception of ω_8 , which is computed 33 cm⁻¹ lower. This is the mode for which Lee *et al.*⁴⁹ observed a much larger basis set effect of no less than 123 cm⁻¹ upon going from 2RCISD/DZP to 2RCISD/TZ2P. (The high basis set sensitivity of this mode was also discussed in detail by Jordan and co-workers.⁶⁹) Perhaps the most crucial difference between the Huzinaga–Dunning DZP set⁷⁰ and the cc-pVDZ basis set is that the carbon *d*-function exponent in the former has a value that is larger than the value optimized for the atomic correlation energy. Since there are two *d* functions in the TZ2P basis set, nonoptimal values for the individual exponents have less severe consequences. This again confirms the suggestion of Martin and Lee⁷¹ that the cc-pVDZ basis set should supplant the Huzinaga–Dunning DZP set in correlated calculations.

With a basis set comparable to the cc-pVTZ one in size, Handy⁵³ still overestimates stretching frequencies by as much as 50 cm⁻¹ at the MP2 level, although the errors for bending frequencies appear to be smaller, and the out-of-plane modes are in fairly good agreement with experiment and our own coupled-cluster calculations. This suggests that higher-order electron correlation is chiefly important for the stretching vibrations, as is to be expected.

The main problem with the density functional results of Handy *et al.*⁵¹ is that CH stretching frequencies are severely underestimated. A significant underestimate is also seen for the CC stretch, while most of the other frequencies are in reasonable agreement with experiment and our calculations.

Finally, the most noteworthy difference between CISD/DZP and 2RCISD/DZP results is perhaps the very significant drop in ω_8 . Other significantly affected modes include ω_2 , ω_3 , ω_4 , and ω_7 .

As for the fundamentals, here again good agreement is seen between CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ values. This would appear to suggest that the anharmonic corrections for both levels of theory are in good agreement as

TABLE III. Computed anharmonic corrections for C₂H₄ (cm⁻¹).

	CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	Expt. Ref. 27	SCF/ DZP Ref. 50
ν_1	147.53	141.16	127	123.2
ν_2	55.41 ^a	50.44 ^a	32	33.8
ν_3	29.14	28.25	28	22.1
ν_4	26.49	20.81	21	20.6
ν_5	149.38	142.99	146	124.3
ν_6	23.31	18.81	23	20.1
ν_7	18.44	17.89	20	14.8
ν_8	15.81	12.43	19	17.1
ν_9	152.45	146.19	129	130.9
ν_{10}	6.17	1.23	17	0.6
ν_{11}	170.63 ^b	160.08 ^b	158	141.1
ν_{12}	39.77	39.35	29	32.3

^aDeperturbed: 46.08 and 44.82 cm⁻¹.

^bDeperturbed: 144.41 and 138.43 cm⁻¹.

well: We see this indeed in Table III. Individual differences are larger than have been seen in previous work (e.g., on CH₄),¹⁵ but the main qualitative features are all correct. Agreement between CCSD(T)/cc-pVTZ and the experimentally derived (GHFF) values is fairly poor, as was to be expected given the evident problems with the GHFF harmonic frequencies. The only other set of anharmonic corrections available is the SCF/DZP calculation by Clabo *et al.*⁵⁰ Differences here are large, and sometimes qualitative rather than quantitative. In that work,⁵⁰ all Fermi type 1 and type 2 interactions for which the gap between the (harmonic) zero-order states is less than 50 cm⁻¹ were taken into account; inspection of the SCF/DZP harmonic frequencies reveals a false Fermi resonance $\omega_3 + \omega_2 \approx \omega_1$, as well as an exaggeratedly large $2\omega_{10} \approx \omega_2$ one, while the important *actual* $\omega_2 + \omega_{12} \approx \omega_{11}$ interaction is not seen at all. This illustrates a main pitfall of using SCF/DZP anharmonic corrections for large molecules together with more sophisticated harmonic frequencies: The more modes the molecule has, the more important resonance interactions will become, and the greater the chance that a low-level treatment will produce qualitatively incorrect anharmonicities due to different underlying resonance structures.

This becomes even clearer when we inspect the individual anharmonicity constants X_{ij} (Table IV). $X_{2,11}$ and $X_{2,12}$ are just two examples of constants that differ qualitatively between the CCSD(T)/cc-pVTZ and SCF/DZP force fields.

We may now compare the Fermi resonance constants with the available experimental values. Our calculated $k_{2,10,10}=26.25$ cm⁻¹ is in excellent agreement with the observed one³² of 27.0 cm⁻¹. For $k_{2,11,12}$, two very different experimental values are available: 113.4 cm⁻¹ determined from analysis of the inertial defect and isotopic shifts,^{29,41} and 44.85 cm⁻¹ determined from local mode analysis.³² Our computed $k_{2,11,12}=125.73$ cm⁻¹ definitely favors the former value. The local mode analysis does assume $k_{2,11,12}=k_{3,11,12}$, which our calculated $k_{3,11,12}=91.74$ cm⁻¹ clearly refutes, but this can still not explain all of the discrepancy between the theoretical and local-mode values. Ad-

TABLE IV. Computed and observed anharmonicity constants (cm⁻¹) of ethylene. (*) Constant affected by Fermi resonance. For the experimental values (Ref. 33), only the asterisks that appear in the original table have been reproduced.

	C ₂ H ₄			Experiment DR Ref. 33	H ₂ CCD ₂	
	CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	SCF/ DZP Ref. 50		CCSD(T)/ cc-pVTZ	Experiment DR Ref. 33
	X _{1,1}	-14.328	-13.740		-12.46	-14.5 ^a
X _{1,2}	-21.737	-21.603	-15.52*	-15.6	-5.353*	-16.6
X _{1,3}	-6.099	-5.579	-6.12*	-11.1 ^b	-0.868	-1.7
X _{1,4}	-6.868	-6.539	-5.83		-6.733	-7.4
X _{1,5}	-60.714	-58.272	-53.11	-57.9 ^a	0.138	-2.1
X _{1,6}	-6.880	-6.769	-5.91	-5.0	-7.165	-7.7
X _{1,7}	-4.650	-4.753	-3.80	-9.0	-1.027	
X _{1,8}	-5.947	-6.464	-4.76	-7.9	-9.154	-6.0
X _{1,9}	-58.607	-56.039	-51.32	-57.9 ^a	-114.089	-116. ^a
X _{1,10}	-3.526	-3.351	-2.64	-5.9	-2.124	~0
X _{1,11}	-57.416	-55.043	-50.09	-57.9 ^a	-0.084	-2.2
X _{1,12}	-5.298	-2.937	+2.56	-11.1 ^b	-5.948	-14.0 ^b
X _{2,2}	-1.329	-1.119	-1.86	-2.3	-4.084*	-1.0
X _{2,3}	-9.638	-9.782	-6.06*	-7.3	-1.925	-7.2
X _{2,4}	-4.083	-3.885	-2.86	-6.5	-2.911	-5.9
X _{2,5}	2.322	3.129	7.24		1.304	
X _{2,6}	-14.284	-15.382	-17.98		-11.645	-12.0
X _{2,7}	-8.006	-7.577	-3.91	-3.2	-2.192	
X _{2,8}	-9.226	-7.694	-4.59	-4.7	-10.136	
X _{2,9}	-2.263	-2.123	-0.73	-0.2	-2.476	-0.2
X _{2,10}	-8.251*	-7.790*	-7.71*	-8.0*	-7.512	-6.7
X _{2,11}	-9.144*	-9.415*	-25.82	-17.3	-4.917	-5.6
X _{2,12}	-2.535*	-3.035*	17.55		-14.859	-11.7
X _{3,3}	-1.178	-1.162	-0.68	-0.9	-2.475	-3.3
X _{3,4}	-3.818	-3.838	-2.78		-0.371	
X _{3,5}	-7.548	-7.233	-6.42	-11.1 ^b	-11.554	-11.2
X _{3,6}	-2.438	-2.348	-2.10		-0.812	
X _{3,7}	-2.528	-2.541	-1.74	-0.8	-2.365	
X _{3,8}	-2.922	-3.919	-2.31		0.044	
X _{3,9}	-7.533	-7.114	-6.51	-11.1 ^b	-0.913	
X _{3,10}	-0.004	2.048	2.43	-4.0	-0.469	+3.2
X _{3,11}	-5.626	-5.196	-3.60	-11.1 ^b	-8.404	-6.6
X _{3,12}	-5.421	-6.358	-6.21	-7.9	+0.854	+0.5
X _{4,4}	-1.918	-1.395	-1.36	-2.4	-0.894	
X _{4,5}	-5.560	-5.054	-4.50		-2.978	-1.7
X _{4,6}	-0.176	1.210	0.36	+4.1	1.237	+2.0
X _{4,7}	-8.473	-8.059	-7.10	-8.9	-2.715	
X _{4,8}	-6.023	-1.933	-5.26	-7.2	-4.829	-2.1
X _{4,9}	-5.960	-5.559	-5.04	-9.5	-5.334	-3.3
X _{4,10}	1.132	1.740	1.34	+2.4	1.236	+2.1
X _{4,11}	-6.939	-6.352	-5.94	-5.0	-4.001	
X _{4,12}	1.464	2.234	1.82		-1.821	-2.8
X _{5,5}	-16.484	-15.841	-14.39	-14.5 ^a	-18.918	-15.5 ^a
X _{5,6}	-1.923	-1.074	3.41	+4.7	-4.257	-3.8
X _{5,7}	-7.725	-7.809	-6.41	-10	-9.800	
X _{5,8}	-9.119	-9.191	-7.62	-10	-0.873	
X _{5,9}	-66.610	-64.303	-58.35	-57.9 ^a	0.215	-0.1
X _{5,10}	-5.354	-5.092	-4.06		0.677	
X _{5,11}	-58.778	-56.041	-51.46	-57.9 ^a	-57.804	-61.8 ^a
X _{5,12}	-11.823	-11.664	-10.08	-11.1 ^b	-0.853	+0.6
X _{6,6}	-0.578	0.046	-0.46	+0.2	-0.304	-0.3
X _{6,7}	1.300	1.868	1.48	-3	1.864	+0.7
X _{6,8}	4.605	7.294	4.21		5.032	+3.8
X _{6,9}	-6.810	-6.299	-4.70	+3.1	-5.805	-5.4
X _{6,10}	-6.446	-5.875	-6.04	-0.2	-1.748	-3.0
X _{6,11}	-5.615	-5.319	-4.46	-4.0	-3.591	-3.1
X _{6,12}	-5.634	-5.101	-6.67	-6.4	-3.280	-2.2
X _{7,7}	0.872	0.977	0.65	+1.2	-0.969	-0.9
X _{7,8}	1.555	0.471	-3.33	+0.2	3.794	+5.0
X _{7,9}	-8.177	-8.299	-7.58	-6.7	-0.943	

TABLE IV. (Continued.)

	C ₂ H ₄			Experiment DR Ref. 33	H ₂ CCD ₂	
	CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	SCF/ DZP Ref. 50		CCSD(T)/ cc-pVTZ	Experiment DR Ref. 33
X _{7,10}	5.951	6.224	5.92	+6.3	2.763	+2.8
X _{7,11}	-4.446	-4.496	-3.17		-4.065	-6.4
X _{7,12}	-5.173	-4.716	-2.53	-3.6 ^c	-1.275	
X _{8,8}	3.224	3.147	0.56	+0.6	1.272	+1.4
X _{8,9}	-8.780	-8.657	-7.64		-15.948	-12.5
X _{8,10}	0.457	1.224	-0.34	+0.9	2.059	
X _{8,11}	-4.905	-4.948	-3.15	-8.0	-1.334	
X _{8,12}	-4.218	-3.627	-1.62	-3.6 ^c	-5.415	
X _{9,9}	-16.449	-15.860	-14.31	-14.5 ^a	-32.021	-29.0 ^a
X _{9,10}	-3.392	-2.867	-1.69	-2.8	-2.538	-3.6
X _{9,11}	-60.144	-57.368	-52.58	-57.9 ^a	-0.018	
X _{9,12}	-10.829	-10.309	-8.50	-11.1 ^b	-14.796	-14.0
X _{10,10}	3.540 [*]	4.597 [*]	4.48 [*]	+2.7 [*]	2.216 [*]	+1.8
X _{10,11}	-3.771	-3.704	-2.83		-2.493	
X _{10,12}	-3.285	-3.401	-3.53	-3.7	-1.074 [*]	-5.3
X _{11,11}	-14.316	-13.626	-12.38	-14.5 ^a	-14.103	-15.5 ^a
X _{11,12}	-14.778 [*]	-14.467 [*]	-29.66	-11.1 ^b	-4.394	-3.4
X _{12,12}	-3.005	-3.832	-4.42	-3.8	-2.618	-4.1

^aConstrained values determined from local mode analysis of the CH stretching manifold.

^bAverage value for anharmonicity constants coupling CH₂ stretching to CH₂ scissoring normal modes.

^cAverage value of both constants.

ditionally, the fact that our computed band origins of 2977.5 (ν_{11}) and 3085.8 ($2\nu_{12}$) err on opposite sides of the experimental values of 2988.6 and 3078.5 cm⁻¹ appears to suggest that our Fermi resonance constant is somewhat too large.

However, as pointed out in Ref. 29, there should be a nontrivial interaction between $\nu_2 + \nu_{12}$ and $2\nu_{10} + \nu_{12}$ as well, which these authors were unable to account for. We here calculate the deperturbed frequency $(2\nu_{10} + \nu_{12})^* = 3085.4$ cm⁻¹, which is indeed very close to the deperturbed $(\nu_2 + \nu_{12})^* = 3062.6$ cm⁻¹. We thence have to deal with a resonance triad of the following form:

$$\begin{pmatrix} (\nu_{11})^* & k_{2,11,12}/\sqrt{8} & K_{10,10,11,12}/2 \\ k_{2,11,12}/\sqrt{8} & (\nu_2 + \nu_{12})^* & k_{2,10,10}/2 \\ K_{10,10,11,12}/2 & k_{2,10,10}/2 & (2\nu_{10} + \nu_{12})^* \end{pmatrix} = \begin{pmatrix} 3000.71 & 44.45 & \approx 0 \\ 44.45 & 3062.55 & 13.26 \\ \approx 0 & 13.26 & 3085.45 \end{pmatrix}. \quad (1)$$

Here, the usual convention (see, e.g., Ref. 72) has been followed, in which a lower-case k denotes a force constant in the original potential and an upper-case K denotes a constant after the contact transformation has been applied. Equation (1) has eigenvalues of 2977.1, 3074.1, and 3097.5 cm⁻¹, the former two of which are both somewhat lower than the experimental ones. This interaction was not accounted for in the local mode analysis, and probably explains at least a substantial part of the discrepancy between computed and local mode $k_{2,11,12}$.

Duncan and Robertson³³ (DR) determined a partial set of anharmonicity constants from the experimental levels, al-

though they applied a number of constraints for the ones involved in the CH stretch local mode polyads. In general, the larger anharmonicity constants agree quite well with our calculations, as do many of the smaller ones. Two groups of constants are constrained in the DR data: The ones involving the stretching manifold are set equal to local mode approximation values, and the anharmonicity constants that couple CH₂ stretching to CH₂ scissoring have been set equal to an average value. While the former approximation appears to hold quite well, this is not true for the latter: Some of our computed ones are significantly higher and others significantly lower. Furthermore, one of the constants ($X_{11,12}$) is involved in the severe $\omega_2 + \omega_{12} \approx \omega_{11}$ resonance: in that light, involving it in an equality constraint with several others does not seem to be a good idea.

DR also give a partial set of anharmonic constants for 1,1-dideuteroethylene. By and large, the same conclusions hold here (Table IV).

Table V lists computed and observed fundamentals for the following deuterated forms of ethylene: C₂H₃D, H₂CCD₂, *cis*-C₂H₂D₂, *trans*-C₂H₂D₂, C₂HD₃, and C₂D₄. The bulk of the experimental data has been taken from the 1973 work of Duncan *et al.*,²⁷ but whenever possible, more recent data have been included (e.g., from the work of the Duncan group on local mode models of the stretching manifolds^{30-32,34}), especially for H₂CCD₂, the fundamentals of which have been studied in some detail.⁴²⁻⁴⁴ (A compilation of available accurate data for C₂H₄ and H₂CCD₂ is given by DR.) Some of the data for C₂HD₃ come from Ref. 27, most of it from the 1988 and 1993 work of the Duncan group on local mode stretching polyads. Unless specifically indi-

TABLE V. Computed and experimental fundamentals (cm⁻¹) for various isotopomers of C₂H₄.

	C ₂ H ₃ D	H ₂ CCD ₂	<i>cis</i> -C ₂ H ₂ D ₂	<i>trans</i> -C ₂ H ₂ D ₂	C ₂ HD ₃	C ₂ D ₄
	Experiment (Ref. 27 unless indicated otherwise)					
ν_1	3028.2 ^m	3017.12 ⁿ	2299	2284	2281.5 ^m	2261.6 ^q
ν_2	1605.5 ^m	1586.05 ^o	1571	1571	1548.0 ^m	1518
ν_3	1288.0 ^m	1029.86 ⁿ	1218	1286	1045	984.6 ^q
ν_4	1000	888.71 ⁿ		988	764	729.958(15) ^f
ν_5	3061.6 ^m	2335.02 ^p	3054	3045	2220.2 ^m	2315.4 ^q
ν_6	1129	1142.27 ⁿ	1044	1004	999	≈1011, ≈1000 ^s
ν_7	808	750.57 ⁿ	842	725.2	725	719.7708(5) ^f
ν_8	943	943.41 ⁿ	763	864	919	780
ν_9	3096.1 ^m	3094.11 ^p	3059	3065	3048.1 ^m	2341.9 ^q
ν_{10}	730	684.64 ⁿ	662	673	≈610	593.3444(9) ^f
ν_{11}	2274.0 ^m	2230.54 ⁿ	2254	2273	2333.5 ^m	2201.0 ^q
ν_{12}	1400.0 ^m	1383.93 ^o	1342	1299	1290	1076.9883(6) ^f
	Calculated					
ν_1	3031.4 ^a	3014.8 ^c	2294.2	2283.0	2277.4 ^j	2260.3
ν_2	1602.1	1582.3	1567.9	1568.5	1544.5	1513.8 ^l
ν_3	1286.0	1029.1	1215.8	1283.0 ^g	1041.8	984.1
ν_4	999.6	890.4	975.0	988.0	757.4	729.2
ν_5	3050.6	2328.0	3050.6 ^d	3040.3 ^h	2217.5	2308.2
ν_6	1121.6	1137.5	1035.7	1000.0	996.0	999.6
ν_7	803.0	746.7	842.4	724.7	724.0	720.0
ν_8	937.5	937.3	754.2	853.0	915.1	768.8
ν_9	3089.9	3087.6	3053.9 ^e	3059.3	3041.5 ^k	2337.1
ν_{10}	728.2	680.9	659.5	669.4	625.6	590.0
ν_{11}	2267.5 ^b	2227.9	2255.4 ^f	2270.4 ⁱ	2327.0	2197.3
ν_{12}	1397.9	1379.8	1338.1	1296.0	1285.6	1075.8

^aResonances with $\nu_2 + \nu_{12}$ at 2992.2; $k_{1,2,12}=96.61$; deperturbed 3001.6; uncorrected 3018.5 cm⁻¹.

^bResonances with $\nu_2 + \nu_{10}$ at 2327.0; $k_{2,10,11}=51.03$; deperturbed 2273.0; uncorrected 2257.6 cm⁻¹.

^cResonances with $2\nu_2$ at 3157.0 ($k_{1,2,2}=72.29$) and $\nu_2 + \nu_{12}$ at 2955.3 ($k_{1,2,12}=85.97$); deperturbed 3008.5; uncorrected 3003.5 cm⁻¹.

^dResonances with $\nu_2 + \nu_{12}$ at 2904.3; $k_{2,5,12}=137.05$; deperturbed 3034.6; uncorrected 3047.3 cm⁻¹.

^eResonances with $2\nu_2$ at 3125.3; $k_{2,2,9}=49.87$; deperturbed 3062.6; uncorrected 2922.6 cm⁻¹.

^fResonances with $\nu_3 + \nu_6$ at 2251.0; $k_{3,6,11}=12.11$; deperturbed 2251.1; uncorrected 2251.6 cm⁻¹.

^gResonances with $2\nu_{10}$ at 1345.0; $k_{3,10,10}=22.29$; deperturbed 1285.1; uncorrected 1281.3 cm⁻¹.

^hResonances with $2\nu_2$ at 3126.9; $k_{2,2,5}=51.81$; deperturbed 3048.1; uncorrected 3012.0 cm⁻¹.

ⁱResonances with $\nu_6 + \nu_{12}$ at 2296.1 ($k_{6,11,12}=-44.70$) and $\nu_2 + \nu_{10}$ at 2335.4 ($k_{2,10,11}=79.43$); deperturbed 2257.7; uncorrected 2165.0 cm⁻¹.

^jResonances with $\nu_3 + \nu_{12}$ at 2327.8 ($k_{1,3,12}=18.53$) and $\nu_6 + \nu_{12}$ at 2282.2 ($k_{1,6,12}=9.45$); deperturbed 2280.3; uncorrected 2276.7 cm⁻¹.

^kResonances with $2\nu_2$ at 3076.9; $k_{2,2,9}=42.30$; deperturbed 3053.4; uncorrected 3064.9 cm⁻¹.

^lResonances with $2\nu_4$ at 1540.6; $k_{2,4,4}=13.89$; deperturbed 1515.6; uncorrected 1510.6 cm⁻¹.

^mReference 34.

ⁿReference 44.

^oReference 43.

^pReference 42.

^qReference 32.

^rReference 73.

^sReference 29.

cated otherwise, accuracy is 1 cm⁻¹ for the older and 0.1 cm⁻¹ for the more recent data.

While running spectroscopic analyses for the various isotopomers we encountered a significant methodological problem. It is far from clear *a priori* which Fermi resonances are to be included in the analysis. The usual empirical criterion—as programmed into SPECTRO—is based on identifying index combinations for which $2\omega_i - \omega_j$ or $\omega_i + \omega_j - \omega_k$ fall below a certain threshold. In the present case, however, this technique failed to identify several resonances which are manifestly present experimentally and, when included, turn out to result in substantial perturbations of the bands involved, while the method also detects several resonances that then turn out to result in insignificant perturbations because the K_{ijj} or K_{ijk} connecting the states are very small. This issue is discussed in detail in Appendix A, where a formula is derived that gives a fairly good estimate

of the difference between explicitly including a Fermi resonance and absorbing it into the anharmonicity constants. This formula has been applied extensively here, and almost invariably appears to identify the correct resonances.

Two Fermi type 2 resonances are found to be present in C₂H₃D: $\nu_2 + \nu_{12} \approx \nu_1$ and $\nu_2 + \nu_{10} \approx \nu_{11}$. Neglecting the former yields a ν_1 that is almost 10 cm⁻¹ too low, while including it puts it 3.2 cm⁻¹ higher than experiment, or in essentially as close agreement as we can reasonably expect. Again, we find disagreement between computed ($k_{1,2,12}=96.61$ cm⁻¹) and observed³⁴ (48.8 ± 7.2 cm⁻¹) Fermi resonance constants. Here, however, a similar equality approximation $k_{1,2,12}=k_{1,3,12}$ was made, which is definitely refuted by our computed $k_{1,3,12}=45.06$ cm⁻¹. Duncan *et al.* do suggest³⁴ the existence of the other resonance, but do not include it in the local mode analysis. Our calculations find that neglecting it brings the computed ν_{11} down by almost 10

TABLE VI. Computed and observed geometry (Å, deg), rotational constants (cm⁻¹), and centrifugal distortion constants (cm⁻¹).

	CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	Best estimate This work ^a	Experiment
$r_e(\text{CC})$	1.351 62	1.337 13	1.331 43	1.330(5) ^b , [1.336] ^c , 1.334(2) ^d
$r_e(\text{CH})$	1.098 41	1.083 18	1.081 38	1.076(5) ^b , [1.076] ^c , 1.081(2) ^d
α_e	121.492	121.453	121.453	—, [120.95] ^c , 121.32(17) ^d
$r_g(\text{CC})$	1.359 60	1.344 87	1.339 19	1.3369(20) ^e
$r_g(\text{CH})$	1.118 89	1.103 69	1.101 89	1.1030(20) ^e
α_g	121.160	121.112	121.112	120.7(6) ^e
$r_z(\text{CC})$	1.358 84	1.344 11	1.338 43	1.335(3) ^b , 1.3384(10) ^d , 1.3391(13) ^f
$r_z(\text{CH})$	1.105 87	1.090 69	1.088 91	1.090(3) ^b , 1.0870(20) ^d , 1.0869(13) ^f
α_z	121.484	121.436	121.436	121.7(4) ^b , 121.32(13) ^d , 121.28(10) ^f
A_e	4.776 77	4.897 55	4.913 87	
B_e	0.976 90	0.999 63	1.007 33	
C_e	0.810 74	0.830 18	0.835 96	
A_0	4.717 35	4.845 87	4.861 96	4.865 96(18) ^g , 4.864 606 4(17) ^h
B_0	0.969 16	0.992 03	0.999 61	1.001 329(61) ^g , 1.001 054 5(5) ^h
C_0	0.801 94	0.821 28	0.826 95	0.828 424(62) ^g , 0.828 042 4(4) ^h
A reduction				
κ	-0.916 00	-1.086 94	-1.087 74	
σ	46.619 11	47.007 39	46.591 86	
$10^6\Delta_J$	1.341 8	1.429 9	1.461 5	1.465 12(65) ^h
$10^6\Delta_K$	75.931 6	81.476 4	81.423 5	86.398 3(150) ^h
$10^6\Delta_{JK}$	9.538 1	10.210 5	10.429 6	10.230 9(48) ^h
$10^6\delta_J$	0.254 1	0.268 7	0.275 0	0.283 55(17) ^h
$10^6\delta_K$	8.984 8	9.5260	9.687 2	10.034 1(103) ^h
10^6R_5	-2.717 9	-2.880 8	-2.934 9	
10^6R_6	-0.019 0	-0.020 0	-0.020 5	
$10^9\Phi_J$	0.001 984	0.002 225	0.002 326	-0.001 668(327) ^h
$10^9\Phi_K$	5.052 604	5.587 881	5.587 630	6.289(82) ^h
$10^9\Phi_{JK}$	0.160 753	0.174 916	0.180 370	0.259 5(245) ^h
$10^9\Phi_{KJ}$	-0.398 414	-0.399 506	-0.404 237	-0.743(85) ^h
$10^9\phi_J$	0.000 950	0.001 048	0.001 090	0.002 955(122) ^h
$10^9\phi_{JK}$	0.092 753	0.101 169	0.104 395	-0.077 7(160) ^h
$10^9\phi_K$	2.969 347	3.277 841	3.338 520	5.409(733) ^h
S Reduction				
10^6D_J	1.254 4	1.328 6	1.357 6	1.447(70) ^g
10^6D_{JK}	10.116 2	10.818 4	11.053 3	14.68(63) ^g
10^6D_K	75.449 7	80.969 8	80.903 7	91.7(16) ^g
10^6d_1	-0.254 1	-0.268 7	-0.275 0	
10^6d_2	-0.048 2	-0.050 7	-0.052 0	
10^6D_J (Wilson)	0.833 7	0.892 5	0.911 4	
10^6D_{JK} (Wilson)	0.711 7	0.754 3	0.772 4	
10^6D_K (Wilson)	0.304 5	0.320 3	0.327 7	
κ	0.916 000	0.916 680	0.915 952	
10^9H_J	0.000 630	0.000 758	0.000 802	
10^9H_{JK}	0.053 407	0.057 381	0.059 497	
10^9H_{KJ}	-0.020 287	0.014 274	0.021 535	
10^9H_K	4.783 177	5.293 102	5.284 256	
10^9h_1	0.000 795	0.000 879	0.000 916	
10^9h_2	0.000 677	0.000 733	0.000 762	
10^9h_3	0.000 155	0.000 168	0.000 174	

^a(*) CCSD(T)/cc-pVTZ force field with empirically corrected (Ref. 7) geometry (see the text).^bReference 46.^cReference 50.^dReference 28.^eReference 75.^fReference 47.^gReference 26.^hReference 38.

cm⁻¹, leaving an error of more than 16 cm⁻¹; including the resonance, however, we nicely meet our goal of 10 cm⁻¹ accuracy. We achieve this level of agreement for all other bands except for ν_5 , where the error is -11.0 cm⁻¹.

All calculated fundamentals for H₂CCD₂ fall within 10 cm⁻¹ of experiment. ν_1 is significantly perturbed, both theoretically (the computed uncorrected ν_1 falls 13.6 cm⁻¹ too low) and experimentally; however, while experiment²⁷ finds

it to be part of a triad involving $\nu_5 + \nu_{10}$ and $\nu_2 + \nu_{12}$ as the other components, theoretically—as in the local mode analysis³⁰—we find it as part of a triad with $2\nu_2$ and $\nu_2 + \nu_{12}$. Including just the Fermi resonance constants in the matrix yields calculated energy levels 2940.4, 3014.8, and 3165.1 cm⁻¹ for $\nu_2 + \nu_{12}$, ν_1 , and $2\nu_2$, respectively, compared to observed levels³⁰ of 2952.3, 3017.1, and 3168.8 cm⁻¹. Again, the agreement between computed ($k_{122}=72.29$, $k_{1,2,12}=85.97$ cm⁻¹) and local mode (35.4 and 40.5 cm⁻¹, respectively) Fermi resonance constants seems disappointing. Given the agreement between computed and observed fundamentals, however, this is probably no great cause for concern. (Much larger deviations would be seen if these constants were really off by a factor of 2.)

In *cis*-C₂H₂D₂, we again find agreement to better than 10 cm⁻¹, except for the missing ν_4 . ν_9 is involved in a particularly severe Fermi resonance with $2\nu_2$, which renders the uncorrected value essentially nonsensical. (The perturbed ν_9 of 3053.9 cm⁻¹ is in as good an agreement with the experimental value²⁷ of 3059 cm⁻¹ as can reasonably be expected.) ν_5 is somewhat perturbed by $\nu_2 + \nu_{12}$, the corrected frequency being 3.3 cm⁻¹ higher (and closer to experiment) than the uncorrected one. Another weak resonance is seen between $\nu_3 + \nu_6 \approx \nu_{11}$; the coupling constant here is very small but the unperturbed states are essentially degenerate.

For *trans*-C₂H₂D₂, we again stay within 10 cm⁻¹ of experiment except for the ν_8 out-of-plane mode (11 cm⁻¹ too low). This time, ν_5 is involved in severe resonance with $2\nu_2$. At least as important—since the uncorrected frequency is clearly nonsensical—is the $\nu_6 + \nu_{12} \approx \nu_{11}$ resonance, which additionally forms a triad with $\nu_2 + \nu_{10}$. (Omitting this third partner increases the difference with experiment from -2.6 to -9.5 cm⁻¹.) Neglecting the higher-order interaction constant $K_{2,6,10,12}$, we obtain 2215.3, 2270.4, and 2303.4 cm⁻¹ as energy levels for the triad. Finally, a weak resonance exists between $2\nu_{10}$ and ν_3 that results in a shift upwards (compared to the uncorrected band) of 1.7 cm⁻¹.

In C₂HD₃, we find a resonance triad involving ν_1 , $\nu_3 + \nu_{12}$, and $\nu_6 + \nu_{12}$, as well as a very strong Fermi type 1 resonance $2\nu_2 \approx \nu_9$. The Fermi resonance constant for the latter is found in local mode studies³⁴ to be 30 ± 12 cm⁻¹; our computed value of 42.30 cm⁻¹ is at the upper corner of the experimental range. Our computed $2\nu_2 = 3091.0$ cm⁻¹ compares very well with the experimental one of 3095.2 cm⁻¹. Since both errors go in the same direction, there is every reason to believe that our Fermi resonance constant is sound. The eigenvalues of the Fermi resonance triad are 2277.2, 2284.4, and 2328.8 cm⁻¹, in the order ν_1 , $\nu_6 + \nu_{12}$, $\nu_3 + \nu_{12}$. Only because two of the three unperturbed states are so close together is any perturbation seen at all: It could as well have been neglected. For the fundamentals of C₂HD₃, 10 cm⁻¹ or better agreement is thus again reached across the board, except for ν_{10} for which only a very approximate experimental value is available.

Finally, for C₂D₄ some very accurate experimental frequencies are available from the work of Mose *et al.*⁷³ Only one Fermi resonance, $2\nu_4 \approx \nu_2$, is seen in the calculations, and accounting for it yields a computed $\nu_2 = 1513.8$ cm⁻¹, in very good agreement with the observed 1518 cm⁻¹. The only

errors above 10 cm⁻¹ are seen for ν_8 , for which the calculated value is 11.2 cm⁻¹ too low, and for ν_6 , where only two approximate experimental values are available: the older one²⁷ being about 11 cm⁻¹ higher than our calculations, the newer one⁷³ being in essentially perfect agreement.

On the whole, we can say that the fundamentals of several isotopomers of C₂H₄ can be reproduced to better than 10 cm⁻¹ if the necessary precautions are taken for the treatment of Fermi resonances. This appears to validate our computed force field by any standard.

As a final note on the anharmonicities: the computed anharmonic zero-point energy of C₂H₄ amounts to 10977.4 cm⁻¹ at the CCSD(T)/cc-pVTZ level, or 31.38 kcal/mol, to which we assign an uncertainty (based on the accuracy of our computed fundamentals) of about 0.1–0.2 kcal/mol. This value should be useful in thermochemical studies.

Computed geometries, rotational constants, and centrifugal distortion constants are found in Table VI. It is clear from the computed rovibrational constants (available as supplementary material⁷⁴ to the paper) that they are fairly reproducible between levels of theory; any differences are primarily due to the different geometries. This would appear to suggest that the effect of zero-point vibration on the geometry would be fairly well reproduced, certainly at levels of theory like CCSD(T)/cc-pVTZ. At this level we find the following r_e geometry: $r_{CC} = 1.3371$ Å; $r_{CH} = 1.0832$ Å; $\theta_{CCH} = 121.45$ degrees. Martin⁷ found that, for a number of reference molecules, single and double bond distances are systematically overestimated at the CCSD(T)/cc-pVTZ level by average amounts of 0.0018 and 0.0057 Å, respectively. This would suggest an empirically corrected r_e geometry of $r_{CC} = 1.3314$ Å; $r_{CH} = 1.0814$ Å; $\theta_{CCH} = 121.45$ degrees, which we would expect to have an error on the order of 0.001 Å. This stands in sharp contrast with the experimentally derived geometry of Clabo *et al.*,⁵⁰ who deduced $r_{CC} = 1.336$ Å; $r_{CH} = 1.076$ Å; $\theta_{CCH} = 120.95$ degrees from the experimental r_0 geometry,²⁶ although it is in marginal agreement with the estimated r_e bond distances of Kuchitsu:⁴⁶ $r_{e,CC} = 1.330 \pm 0.005$ Å; $r_{e,CH} = 1.076 \pm 0.005$ Å, as well as in good agreement, except for the shorter CC bond distance, with Duncan's estimated r_e structure²⁸ of $r_{e,CC} = 1.334 \pm 0.002$ Å, $r_{e,CH} = 1.081 \pm 0.002$ Å, and $\theta_{e,CCH} = 121.32 \pm 0.17$ degrees. Not only is the kind of error with respect to the Clabo *et al.* extrapolated geometry totally out of character with results for other molecules,⁷ the difference between their corrected r_{CC} and its uncorrected CCSD(T)/cc-pVTZ counterpart goes against the trend of CCSD(T) to overestimate, rather than underestimate, bond distances.

For small changes in the geometry, we can roughly assume that the force field will remain unchanged. If we now substitute our empirically corrected geometry into the spectroscopic analysis for the CCSD(T)/cc-pVTZ force field, we find the following ground-state rotational constants: $A_0 = 4.86196$; $B_0 = 0.99961$; $C_0 = 0.82695$ cm⁻¹, which are in excellent agreement with the observed rotational constants:²⁷ $A_0 = 4.86596(18)$; $B_0 = 1.001329(61)$; $C_0 = 0.828424(62)$ cm⁻¹. Error propagation reveals that changes on the order of 0.001 Å in r_{CH} and 0.05 degrees in θ_{CCH} are sufficient to produce deviations substantially larger

TABLE VII. Computed and experimentally derived quadratic force constants in symmetry coordinates. Units are consistent with aJ for energy, Å for distances, and radian for angles.

	CCSD(T)/ cc-pVDZ This work	CCSD(T)/ cc-pVTZ This work	2RCISD/ TZ2P Ref. 49	SCF/ 73/3+1 Ref. 76	Duncan <i>et al.</i> Ref. 27	Duncan & Hamilton Ref. 29	Kuchitsu <i>et al.</i> Ref. 76
$F_{1,1}$	5.640 80	5.626 03	5.8974	5.950	5.638(27)	5.630(24)	5.169
$F_{2,1}$	0.123 75	0.156 66	0.1862	0.192	0.365(56)	0.160(38)	0.427
$F_{2,2}$	9.410 26	9.393 20	9.5696	9.939	9.395(38)	9.418(38)	9.519
$F_{3,1}$	-0.139 65	-0.135 27	-0.1367	-0.116	+0.090(42)	-0.125(31)	+0.087
$F_{3,2}$	0.501 68	0.520 06	0.5243	0.546	0.501(14)	0.528(17)	0.554
$F_{3,3}$	1.490 89	1.478 08	1.5586	1.479	1.242(6)	1.2435(51)	1.248
$F_{4,4}$	0.276 57	0.277 87	0.2816	0.331	0.276(2)	0.277(2)	0.281
$F_{5,5}$	5.597 41	5.544 81	5.8181	5.854	5.657(34)	5.514(27)	5.465
$F_{6,5}$	0.211 56	0.202 30	0.1907	0.208	0.365(33)	0.220(18)	0.180
$F_{6,6}$	0.640 42	0.637 54	0.6669	0.622	0.560(3)	0.5502(37)	0.569
$F_{7,7}$	0.200 92	0.202 88	0.2033	0.252	0.204(1)	0.205(2)	0.207
$F_{8,8}$	0.136 60	0.143 05	0.1403	0.184	0.148(1)	0.147(1)	0.149
$F_{9,9}$	5.627 32	5.582 89	5.8444	5.904	5.493(24)	5.525(28)	5.498
$F_{10,9}$	0.070 00	0.075 09	0.0731	0.088	-0.161(42)	-0.116(40)	-0.279
$F_{10,10}$	0.462 83	0.453 77	0.4813	0.445	0.413(4)	0.4108(37)	0.417
$F_{11,11}$	5.630 84	5.612 59	5.8751	5.936	5.603(25)	5.580(24)	5.528
$F_{12,11}$	-0.198 77	-0.190 05	-0.1855	-0.177	-0.147(19)	-0.142(13)	+0.087
$F_{12,12}$	1.371 17	1.366 79	1.4336	1.356	1.152(6)	1.1514(60)	1.191

than those seen; B_0 and C_0 are somewhat less affected by changes in r_{CC} (of which A_e is independent). Therefore, we can assume that our empirically corrected geometry possesses uncertainties on the order of ± 0.001 Å for the bond distances, and less than ± 0.1 degrees for the angle.

Using the computed anharmonic force field information, we find an r_g geometry of $r_{CC}=1.3392$ Å; $r_{CH}=1.1019$ Å; $\theta_{CCH}=121.11$ degrees, to be compared with the observed one:⁷⁵ $r_{CC}=1.3369(20)$ Å; $r_{CH}=1.1030(20)$ Å; $\theta=120.7(6)$ degrees. The r_z geometry, on the other hand, is computed to be $r_{CC}=1.3384$ Å; $r_{CH}=1.0889$ Å; $\theta_{CCH}=121.44$ degrees, compared to Kuchitsu's experimental determination⁴⁶ of $r_{CC}=1.3348(30)$ Å; $r_{CH}=1.0902(30)$ Å; $\theta=121.7(4)$ degrees. So while the CH bond distance and the bond angle are both within the uncertainty of the experimental values, our CC bond distance suggests a somewhat longer value; indeed, more recent experiments by Hirota *et al.*⁴⁷ yield $r_{z,CC}=1.3391(13)$ Å, $r_{z,CH}=1.0869(13)$ Å, and $\theta_{CCH}=121.28(10)$ degrees, in very good agreement with our calculations. The results of Hirota *et al.* suggest our computed bond angle might be slightly too small and our r_{CH} slightly too long: their effect on the rotational constants are opposite, and might cancel each other.

On the whole, we believe our empirically corrected or estimated r_e geometry is considerably more accurate than previous experimental and experimentally derived ones.

Computed quartic and sextic centrifugal distortion constants, both in the A and S reductions, have been given in Table VI, together with the experimental information available. One chief factor in the dependence of these constants on the level of theory is of course the quality of the reference geometry: We have therefore also provided values using the CCSD(T)/cc-pVTZ force field together with our empirically corrected geometry. Among the S reduction constants, the extreme sensitivity of H_{KJ} to the level of theory should be noted: It even changes sign between the CCSD(T)/cc-pVDZ

and CCSD(T)/cc-pVTZ levels of theory. The available experimental quartic centrifugal constants of Van Lerberghe *et al.*²⁶ approximate the molecule as a symmetric top (i.e., it is treated in the S reduction, but with d_1 and d_2 constrained to zero), so a useful comparison is not really possible. Cauuet *et al.*,³⁸ however, determined up to sextic centrifugal constants in the A reduction. Of these, the quartic centrifugal constants are in reasonable (for the large Δ_K and for δ_K) to excellent agreement with our calculations: any deviations will be partly due to the second-order perturbation theory approximation, partly to vibrational effects (since we are comparing calculated Δ_e with observed Δ_0 values). The same explanations apply for the sextic constants, which are in much less good agreement but are also much less well-defined experimentally. (In this context, it should be noted that even the rotational constants differ by as much as the third digit from a previous determination²⁶—a difference well in excess of the quoted statistical uncertainties.)

Cauuet *et al.*³⁸ found first-order Coriolis interactions with the following interaction constants in their analysis: $\xi_{4,10}^B=1.794(1)$, $\xi_{7,10}^a=-4.426(11)$, $\xi_{4,12}^a=-5.2324$, $\xi_{7,12}^b=1.7392$, and $\xi_{10,12}^c=-0.137 64$ cm⁻¹. The larger ones of these are in good agreement with our calculated values from the CCSD(T)/cc-pVTZ force field: 1.744 51, -4.908 93, -5.299 48, 1.729 89, and -0.067 79 cm⁻¹. Any deviations between computed and experimental values should largely be chalked up to higher-order terms in the Coriolis interaction. The calculations additionally find $\xi_{3,6}^c=-0.601 35$ cm⁻¹. It should be noted that, similar to the case of Fermi resonance, a resonance criterion based on $\omega_i - \omega_j$ fails to find several important Coriolis interactions, notably those involving ν_{12} . An improved resonance criterion is outlined in Appendix B.

Table VII contains computed and experimentally derived quadratic force constants in symmetry coordinates, while a complete listing of the CCSD(T)/cc-pVTZ cubic and quartic

force constants in symmetry coordinates is available as supplementary material⁷⁴ to the paper. The quadratic force field appears to be in qualitative, but not quantitative, agreement between the CCSD(T)/cc-pVTZ and 2RCISD/TZ2P levels. Agreement between the CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVTZ quadratic force fields is remarkably good, which was expected given the good agreement between the computed harmonic frequencies. Agreement with the experimentally derived force fields predictably is good for the irreducible representations that contain only one mode, but qualitative differences are seen for the others, especially in the A_g block. The interaction force constants in particular differ by as much as a factor of 2, or even have opposite signs, in the 1973 Duncan determination;²⁷ most of these problems, however, are resolved in the 1981 Duncan refinement,²⁹ with $F_{9,10}$ remaining as the main difference. Interestingly, the small-basis set SCF calculation by Pulay and Meyer⁷⁷ is in qualitative agreement with the present calculations, even if—as expected—the actual values for some of the force constants differ considerably due to basis set incompleteness and complete neglect of electron correlation. Given the considerable difficulty involved in solving an inverse eigenvalue problem with this number of parameters, and given the excellent agreement with experiment that we find for our calculated CCSD(T)/cc-pVTZ vibrational frequencies, we can safely consider our force constants to be more reliable.

In order to encourage further experimental work on the isotopomers, the following are made available as supplementary material to the paper:⁷⁴ (a) a table with computed r_g and r_z geometries, as well as rotational and centrifugal distortion constants; (b) a table with rovibrational coupling constants; and (c) a table with anharmonicity constants. All these tables cover all deuterated forms of ¹²C₂H₄.

IV. CONCLUSIONS

The quartic force field of C₂H₄ has been computed *ab initio* using augmented coupled cluster methods and basis sets of *spdf* quality. We have found the following:

—for seven different isotopomers, computed and observed fundamentals generally agree to within 10 cm⁻¹ or better;

—deviations between computed and experimentally derived harmonic frequencies are substantially larger, due to approximations in the determination of the experimental values;

—some fundamentals of several of the isotopomers studied are involved in fairly complicated resonance polyads;

—an empirically corrected r_e geometry is proposed that is shown to be accurate to ±0.001 Å and ±0.1 degrees by an analysis involving computed zero-point motion corrections and comparison of computed and observed ground-state rotational constants;

—CCSD(T)/cc-pVDZ results are in surprisingly good agreement with experiment given the small basis set;

—the well-known basis set effect for the CH₂ twist mode ν_8 is much smaller using correlation consistent basis sets than previously reported for Huzinaga–Dunning type basis sets;

—improved diagnostics for the magnitude of Coriolis and Fermi resonance perturbations have been proposed;

—summarizing, the first-ever accurate determination of the anharmonic force field of a molecule with more than five atoms has been made.

ACKNOWLEDGMENTS

J.M. thanks the National Science Foundation of Belgium (NFWO/FNRS) for a Postdoctoral Fellowship. This research was supported by the National Science Foundation through Cooperative Agreement DASC-8902825 and by Grant No. CHE-9320718 (P.R.T.). The C90 calculations were performed under a grant of computer time from the San Diego Supercomputer Center. J.M. and J.P.F. are indebted to the Prime Minister's Office for Science Policy Programming (DPWB) for Grant No. IUAP-48 (Characterization of Materials) which enabled the purchase of the IBM RS/6000 model 365 workstations. The present work forms part of project IT/SC 11 (Supercomputing) of the DPWB. The authors finally wish to acknowledge Professor H. J. Geise (U. of Antwerp), Professor L. Lathouwers (*ibid.*), and Professor J. Liévin (Université Libre de Bruxelles) for helpful discussions.

APPENDIX A: AN IMPROVED DIAGNOSTIC FOR SIGNIFICANT PERTURBATION BY FERMI RESONANCE

Second-order rovibrational perturbation theory packages such as SPECTRO⁶⁸ identify strong Fermi resonances by small values of $\Delta=2\omega_i-\omega_k$ for Fermi type 1 or $\Delta=\omega_i+\omega_j-\omega_k$ for Fermi type 2 resonances.

The second-order perturbation theory expressions for the anharmonicity constants of an asymmetric top are well known to be^{66,78}

$$X_{ii} = \phi_{iii}/16 - \sum_k \frac{\phi_{iik}^2(8\omega_i^2 - 3\omega_k^2)}{16\omega_k(4\omega_i^2 - \omega_k^2)}, \quad (\text{A1})$$

$$X_{ij} = \phi_{iij}/4 - \sum_k \phi_{iik}\phi_{jjk}/4\omega_k - \sum_k \phi_{ijk}^2 \frac{\omega_k(\omega_i^2 + \omega_j^2 - \omega_k^2)}{2\Omega_{ijk}} + \sum_\alpha B_\alpha(\xi_{ij}^\alpha)^2 \left(\frac{\omega_i}{\omega_j} + \frac{\omega_j}{\omega_i} \right) \quad (\text{A2})$$

in which

$$\Omega_{klm} \equiv (\omega_k + \omega_l + \omega_m)(-\omega_k + \omega_l + \omega_m)(\omega_k - \omega_l + \omega_m) \times (\omega_k + \omega_l - \omega_m), \quad (\text{A3})$$

and where the energy levels (relative to the ground state) have the usual expression

$$G = \sum_r \omega_r n_r + \sum_r X_{rr}(n_r^2 + n_r) + \sum_{s>r} X_{rs} \left[n_r n_s + \frac{1}{2}(n_r + n_s) \right], \quad (\text{A4})$$

$$\nu_i = \omega_i + 2X_{ii} + \sum_{r \neq i} \frac{X_{ir}}{2}, \quad (\text{A5})$$

$$(2\nu_i) = 2\omega_i + 6X_{ii} + \sum_{r \neq i} X_{ir}, \quad (\text{A6})$$

$$\begin{aligned} \nu_i + \nu_j &= \omega_i + \omega_j + 2X_{ii} + 2X_{jj} + 2X_{ij} \\ &+ \frac{1}{2} \sum_{r \neq \{i,j\}} (X_{ir} + X_{jr}). \end{aligned} \quad (\text{A7})$$

In cases where $2\omega_i \approx \omega_k$ (Fermi type 1 resonance) or $\omega_i + \omega_j \approx \omega_k$ (Fermi type 2 resonance), the expressions for $\{X_{ii}, X_{ik}\}$ and $\{X_{ij}, X_{ik}, X_{jk}\}$, respectively, contain near-singular terms corresponding to these interactions. In the diagonal anharmonicity constants, the offending term can be factored as

$$\frac{\phi_{iik}^2(8\omega_i^2 - 3\omega_k^2)}{\omega_k(4\omega_i^2 - \omega_k^2)} = \frac{\phi_{iik}^2}{2} \left(\frac{1}{2\omega_i + \omega_k} + \frac{4}{\omega_k} - \frac{1}{2\omega_i - \omega_k} \right), \quad (\text{A8})$$

and for their off-diagonal counterparts as

$$\begin{aligned} \phi_{ijk}^2 \frac{\omega_k(\omega_i^2 + \omega_j^2 - \omega_k^2)}{\Omega_{ijk}} \\ = \frac{\phi_{ijk}^2}{4} \left(\frac{1}{\omega_i + \omega_j + \omega_k} + \frac{1}{-\omega_i + \omega_j + \omega_k} \right. \\ \left. + \frac{1}{\omega_i - \omega_j + \omega_k} - \frac{1}{\omega_i + \omega_j - \omega_k} \right), \end{aligned} \quad (\text{A9})$$

where in both expressions the near-singularity has been isolated in the last term. If we now delete these final terms, we obtain expressions for the deperturbed anharmonicity constants. This is exactly equivalent (see, e.g., Ref. 77) to ignoring this particular interaction in the contact transformation: The actual energy levels are then found by finding the eigenvalues of the matrix

$$\begin{pmatrix} 2\nu_i & \phi_{iik}/4 \\ \phi_{iik}/4 & \nu_k \end{pmatrix} \quad (\text{A10})$$

for type 1 resonances [remembering that $k_{iik} = \phi_{iik}/2$, where k is used for force constants in the restricted summation (Nielsen) form of the potential and ϕ for force constants in the unrestricted summation form] and

$$\begin{pmatrix} \nu_i + \nu_j & \phi_{ijk}/\sqrt{8} \\ \phi_{ijk}/\sqrt{8} & \nu_k \end{pmatrix} \quad (\text{A11})$$

for type 2 resonances. Denoting the average frequency of the deperturbed states by $\bar{\nu}$ and the separation by $\bar{\Delta}$, it is easily shown that the eigenvalues of the matrices are given by

$$\nu = \bar{\nu} \pm \frac{\bar{\Delta}}{2} \sqrt{1 + \frac{\phi_{iik}^2}{4\bar{\Delta}^2}} \quad (\text{A12})$$

for type 1 and

$$\nu = \bar{\nu} \pm \frac{\bar{\Delta}}{2} \sqrt{1 + \frac{\phi_{ijk}^2}{2\bar{\Delta}^2}} \quad (\text{A13})$$

for type 2 resonances.

The connection between these expressions and the terms deleted from the anharmonicity constants is easily found. If we consider the diagonal terms to be the zero-order states and the off-diagonal ones to be a perturbation, then it becomes obvious that the perturbation expansion only has terms at even orders, and that the second-order term is given by $\phi_{iik}^2/16\bar{\Delta}$ for type 1 cases and $\phi_{ijk}^2/8\bar{\Delta}$ for type 2 cases. (Incidentally, successive even orders in perturbation theory exactly correspond to successive terms in the Taylor series expansion of $\sqrt{1+x^2}$, where $x \equiv \phi_{iik}/2\bar{\Delta}$ for type 1, or $\phi_{ijk}/\sqrt{2}\bar{\Delta}$ for type 2 resonances.)

What would the effect of including the near-singular interaction in the energy level expressions instead have been? We will consider the case of a Fermi type 1 resonance, $2\omega_i \approx \omega_k$. With

$$X_{ii} - X_{ii}^* = -\frac{\phi_{iik}^2}{32} \left(\frac{-1}{2\omega_i - \omega_k} \right) = \frac{\phi_{iik}^2}{32\Delta}, \quad (\text{A14})$$

$$X_{ik} - X_{ik}^* = -\frac{\phi_{iki}^2}{8} \left(\frac{+1}{\omega_i - \omega_k + \omega_i} \right) = \frac{-\phi_{iik}^2}{8\Delta}, \quad (\text{A15})$$

(in which the asterisks denote deperturbed term values or constants) we find

$$\begin{aligned} (2\nu_i) - (2\nu_i)^* &= 6(X_{ii} - X_{ii}^*) + (X_{ik} - X_{ik}^*) \\ &= \left(\frac{6}{32} - \frac{1}{8} \right) \frac{\phi_{iik}^2}{\Delta} = \frac{\phi_{iik}^2}{16\Delta}, \end{aligned} \quad (\text{A16})$$

$$\nu_k - \nu_k^* = \frac{1}{2} (X_{ik} - X_{ik}^*) = \frac{-\phi_{iik}^2}{16\Delta}, \quad (\text{A17})$$

$$[(2\nu_i) - \nu_k] - [(2\nu_i)^* - \nu_k^*] = \frac{\phi_{iik}^2}{8\Delta}, \quad (\text{A18})$$

where the fact that both corrections (A16) and (A17) have the same absolute value but opposite sign serves as a check on our calculation. This result, if we take $\Delta \approx \bar{\Delta}$, is equivalent to the second-order term of Eq. (A12)!

The equivalence can be shown analogously in the case of a Fermi type 2 resonance. We have here

$$X_{ij} - X_{ij}^* = \frac{-\phi_{ijk}^2}{8} \left(\frac{-1}{\omega_i + \omega_j - \omega_k} \right) = \frac{\phi_{ijk}^2}{8\Delta}, \quad (\text{A19})$$

$$X_{ik} - X_{ik}^* = \frac{-\phi_{ikj}^2}{8} \left(\frac{1}{\omega_i - \omega_k + \omega_j} \right) = \frac{-\phi_{ijk}^2}{8\Delta}, \quad (\text{A20})$$

$$X_{jk} - X_{jk}^* = \frac{-\phi_{jki}^2}{8} \left(\frac{1}{\omega_j - \omega_k + \omega_i} \right) = \frac{-\phi_{ijk}^2}{8\Delta}, \quad (\text{A21})$$

$$\begin{aligned}
 (\nu_i + \nu_j) - (\nu_i + \nu_j)^* &= 2(X_{ij} - X_{ij}^*) + \frac{1}{2} [(X_{ik} - X_{ik}^*) \\
 &\quad + (X_{jk} - X_{jk}^*)] \\
 &= \frac{\phi_{ijk}^2}{4\Delta} - \frac{\phi_{ijk}^2}{8\Delta} = \frac{\phi_{ijk}^2}{8\Delta}, \quad (\text{A22})
 \end{aligned}$$

$$\nu_k - \nu_k^* = \frac{1}{2} [(X_{ik} - X_{ik}^*) + (X_{jk} - X_{jk}^*)] = \frac{-\phi_{ijk}^2}{8\Delta}, \quad (\text{A23})$$

which again corresponds exactly to the leading term of Eq. (A13) if we assume $\Delta \approx \bar{\Delta}$.

The difference between Eq. (A12) (with $\bar{\Delta} \approx \Delta$) and Eq. (A16)—or between Eqs. (A13) and (A22)—is then a good measure for higher-order effects or, more specifically, of whether or not it is worth the effort to explicitly include the resonance involved

$$\text{effect} = \frac{\Delta}{2} \left(\sqrt{1 + \frac{\phi_{iik}^2}{4\Delta^2}} - 1 - \frac{\phi_{iik}^2}{8\Delta^2} \right) = -\frac{\phi_{iik}^4}{256\Delta^3} + \dots \quad (\text{A24})$$

for type 1 and

$$\text{effect} = \frac{\Delta}{2} \left(\sqrt{1 + \frac{\phi_{ijk}^2}{2\Delta^2}} - 1 - \frac{\phi_{ijk}^2}{4\Delta^2} \right) = -\frac{\phi_{ijk}^4}{64\Delta^3} + \dots \quad (\text{A25})$$

for type 2 resonances. It is readily seen that the effect is strongly dependent on the magnitude of the Fermi resonance constant, relative to the state splitting. Therefore, a test for Fermi resonance based simply on Δ being below a certain threshold does not necessarily provide a reliable indication of whether or not a specific resonance should be included. In the present work, the resonance $2\omega_2 \approx \omega_1$ in H₂CCD₂ is a good example. Δ here has the relatively large value of 187 cm⁻¹, but the very large $\phi_{122} = 144.6$ cm⁻¹ causes a pronounced perturbation.

APPENDIX B: AN IMPROVED CRITERION FOR SIGNIFICANT CORIOLIS RESONANCE

Like for Fermi resonance, simply the frequency difference $\omega_i - \omega_j$ is not always a reliable indication for significant Coriolis resonances, as we could amply verify for C₂H₄. We will therefore derive a different criterion here.

The effect of that particular interaction on the rovibrational coupling constant $\alpha_{i\beta}$ is

$$\Delta\alpha_{i\beta} = \frac{2B_\beta^2}{\omega_i} (\zeta_{ij}^\beta)^2 \frac{3\omega_i^2 + \omega_j^2}{\omega_i^2 - \omega_j^2}. \quad (\text{B1})$$

In case of Coriolis interaction this term is replaced by⁷⁷

$$\Delta\alpha_{i\beta}^* = \frac{-B_\beta^2}{\omega_i} (\zeta_{ij}^\beta)^2 \frac{(\omega_i - \omega_j)^2}{\omega_j(\omega_i + \omega_j)}. \quad (\text{B2})$$

The difference is

$$\alpha_{i\beta} - \alpha_{i\beta}^* = \frac{2B_\beta^2}{\omega_i} (\zeta_{ij}^\beta)^2 \left[\frac{3\omega_i^2 + \omega_j^2}{(\omega_i + \omega_j)(\omega_i - \omega_j)} + \frac{\omega_i^2 - 2\omega_i\omega_j + \omega_j^2}{2\omega_j(\omega_i + \omega_j)} \right] \quad (\text{B3})$$

$$= \frac{B_\beta^2}{\omega_i\omega_j} (\zeta_{ij}^\beta)^2 \frac{(\omega_i + \omega_j)^2}{(\omega_i - \omega_j)}. \quad (\text{B4})$$

We see that the effect depends quadratically on the Coriolis interaction constant and on the rotational constant involved, and only inversely on the difference in harmonic frequencies.

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