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Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields

P. J. Stephens* and F. J. Devlin

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

C. F. Chabalowski

U.S. Army Research Laboratory, AMSRL-WT-PC, Aberdeen Proving Ground, Maryland 21005-5066

M. J. Frisch

Lorentzian Inc., 140 Washington Ave., North Haven, Connecticut 06473

The unpolarized absorption and circular dichroism spectra of the fundamental vibrational transitions of the chiral molecule 4-methyl-2-oxetanone are calculated *ab initio*. Harmonic force fields are obtained using density functional theory (DFT), MP2 and SCF methodologies, and a [5s4p2d/3s2p] (TZ2P) basis set. DFT calculations use the LSDA, BLYP, and Becke3LYP (B3LYP) density functionals. Mid-IR spectra predicted using LSDA, BLYP, and B3LYP force fields are of significantly different quality, the B3LYP force field yielding spectra in clearly superior, and overall excellent, agreement with experiment. The MP2 force field yields spectra in slightly worse agreement with experiment than the B3LYP force field. The SCF force field yields spectra in poor agreement with experiment. The basis set dependence of B3LYP force fields is also explored: the 6-31G* and TZ2P basis sets give very similar results while the 3-21G basis set yields spectra in substantially worse agreement with experiment.

The use of density functional theory (DFT) in the *ab initio* calculation of molecular properties has recently increased dramatically.[1] This can be attributed to (1) the development of new and more accurate density functionals, (2) the increasing versatility, efficiency, and availability of DFT codes, and, most importantly, (3) the superior ratio of accuracy to effort exhibited by DFT computations relative to other *ab initio* methodologies.

We focus here on the application of DFT to the prediction of vibrational spectra. With the most accurate density functionals currently in use, DFT predicts harmonic vibrational frequencies of substantially higher accuracy than obtained via SCF calculations and of similar accuracy to the predictions of MP2 calculations.[2] Since DFT calculations are substantially less demanding computationally than MP2 calculations, it is clear that DFT offers significant advantages in predicting harmonic vibrational force fields, frequencies, and spectra.

In particular, DFT promises to greatly facilitate the calculation of vibrational circular dichroism (VCD) spectra.[3] Experience[4] has shown that (with the exception of small, symmetrical molecules) SCF harmonic force fields are generally of insufficient accuracy to provide useful predictions of VCD spectra. Calculations using MP2 harmonic force fields are substantially

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* To whom correspondence should be addressed.
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more successful[4c,5] but also much more demanding. The lower computational demands of DFT suggest that DFT may become preferred over the MP2 methodology in future *ab initio* predictions of VCD spectra.

We report here calculations of the unpolarized absorption and circular dichroism spectra arising from the fundamental vibrational excitations of the chiral molecule 4-methyl-2-oxetanone, **1**, previously studied (both experimentally and theoretically) in

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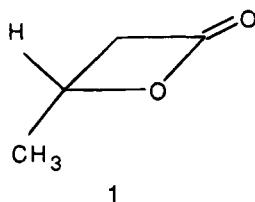
our laboratories.[4b,6] We compare the accuracies of spectra predicted using DFT, MP2, and SCF harmonic force fields. The accuracy of DFT calculations is dependent on the density functional employed. In this work, we compare three significantly different density functionals: LSDA, BLYP, and Becke3LYP. The LSDA and BLYP functionals have been widely used.[1,2] The Becke3LYP functional is a hybrid of several components, whose relative weights are chosen by reference to experimental thermochemical data. The accuracies of such hybrid functionals in predicting molecular geometries and vibrational frequencies have not yet been thoroughly characterized.

Our calculations take advantage of recent developments in the computation of DFT and MP2 harmonic force fields *via* analytical derivative techniques.[7]

Methods

Harmonic force fields for **1** were calculated *ab initio* at SCF and MP2 levels and using DFT via GAUSSIAN 92 and GAUSSIAN 92/DFT.[8] All force fields were calculated using analytical derivative methods.[7] DFT calculations were carried out using three density functionals:

1. LSDA (local spin density approximation). This uses the standard local exchange functional[9] and the local correlation functional of Vosko, Wilk, and Nusair (VWN).[10]

2. BLYP. This combines the standard local exchange functional with the gradient correction of Becke[9] and uses the Lee—Yang—Parr correlation functional (which also includes density gradient terms).[11]

3. Becke3LYP. This functional is a hybrid of exact (Hartree—Fock) exchange with local and gradient-corrected exchange and correlation terms, as first suggested by Becke.[12] The exchange-correlation functional proposed and tested by Becke was

$$E_{xc} = (1 - a_0)E_x^{LSDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} +$$
$$E_c^{LSDA} + a_c \Delta E_c^{PW91} \quad (1)$$

Here ΔE_x^{B88} is Becke's gradient correction to the exchange functional, and ΔE_c^{PW91} is the Perdew—Wang gradient correction to the correlation functional.[13] Becke suggested coefficients $a_0 = 0.2$, $a_x = 0.72$, and $a_c = 0.81$ based on fitting to heats of formation of small molecules. Only single-point energies were involved in the fit; no molecular geometries or frequencies were used. The Becke3LYP functional in Gaussian 92/DFT uses the values of a_0, a_x, and a_c suggested by Becke but uses LYP for the correlation functional. Since LYP does not have an easily separable local component, the VWN local correlation expres-

sion has been used to provide the different coefficients of local and gradient corrected correlation functionals:

$$E_{xc}^{B3LYP} = (1 - a_0)E_x^{LSDA} + a_0 E_x^{HF} + a_x \Delta E_x^{B88} +$$
$$a_c E_c^{LYP} + (1 - a_c)E_c^{VWN} \quad (2)$$

(Note that, in contrast to eq 1, the accuracy of eq 2 in predicting thermochemical properties has not yet been characterized.) The standard fine grid in Gaussian 92/DFT[14] was used in all DFT calculations. This grid was produced from a basic grid having 75 radial shells and 302 angular points per radial shell for each atom and by reducing the number of angular points for different ranges of radial shells, leaving about 7000 points per atom while retaining similar accuracy to the original (75, 302) grid. Becke's numerical integration techniques[15] were employed.

Atomic polar tensors (APTs)[16] were calculated at the same time as harmonic force fields. Atomic axial tensors (AATs)[16] were calculated using the distributed origin gauge,[16,17] in which the AAT of nucleus λ, $(M_{\alpha\beta}^\lambda)^0$, with respect to origin O is given by

$$(M_{\alpha\beta}^\lambda)^0 = (I_{\alpha\beta}^\lambda)^\lambda + \frac{i}{4\hbar c}\sum_{\gamma\delta}\epsilon_{\beta\gamma\delta}R_{\lambda\gamma}^0 P_{\alpha\delta}^\lambda \quad (3)$$

where R_λ^0 is the equilibrium position of nucleus λ relative to origin O, $P_{\alpha\beta}^\lambda$ is the APT of nucleus λ, and $(I_{\alpha\beta}^\lambda)^\lambda$ is the electronic AAT of nucleus λ calculated with the origin at R_λ^0. "Local" AATs, $(I_{\alpha\beta}^\lambda)^\lambda$, are calculated using CADPAC (version 5)[18] at the SCF level. (At the present time neither MP2 nor DFT codes for AATs are available.)

Vibrational frequencies, dipole strengths, and rotational strengths were calculated from the harmonic force fields, APTs, and AATs.[19] Unpolarized absorption and circular dichroism spectra were synthesized thence using Lorentzian band shapes.[20] Calculations used 3-21G,[21] 6-31G*,[21] and [5s4p2d/3s2p], TZ2P[16] basis sets (66, 102, and 228 basis functions, respectively). SCF and MP2 calculations were carried out using the San Diego Supercomputer Center CRAY-YMP and C90 machines. DFT calculations were carried out at Lorentzian Inc. using IBM RS/6000-590 and SGI Challenge machines.

Results and Discussion

Unpolarized absorption and circular dichroism spectra of **1**, measured in CS_2 and CCl_4 solutions,[6] are reproduced in Figures 1 and 2 over the spectral range 650—1500 cm^{-1}. Frequencies, dipole strengths, and rotational strengths of transitions assigned to fundamental excitations, obtained by Lorentzian fitting of the experimental spectra,[6] are given in Table 1. The spectra attributable to these transitions alone are also shown in Figures 1 and 2.

Harmonic frequencies, dipole strengths, and rotational strengths have been calculated for **1** using DFT at the TZ2P basis set level and utilizing the LSDA, BLYP, and B3LYP density functionals. Unpolarized absorption spectra and VCD spectra derived thence are displayed in Figures 1 and 2. The absorption and VCD spectra predicted using the LSDA, BLYP, and B3LYP functionals are substantially different, demonstrating that the choice of functional is of importance. Comparison to the fundamental absorption and VCD spectra shows that the B3LYP functional provides spectra in best agreement with experiment when judged on the basis of the qualitative pattern of frequencies and intensities. The BLYP and LSDA functionals yield spectra in significantly worse agreement. The variations among predicted spectra originate predominantly in the variations in the harmonic force fields. (Variations in the APTs are of minor
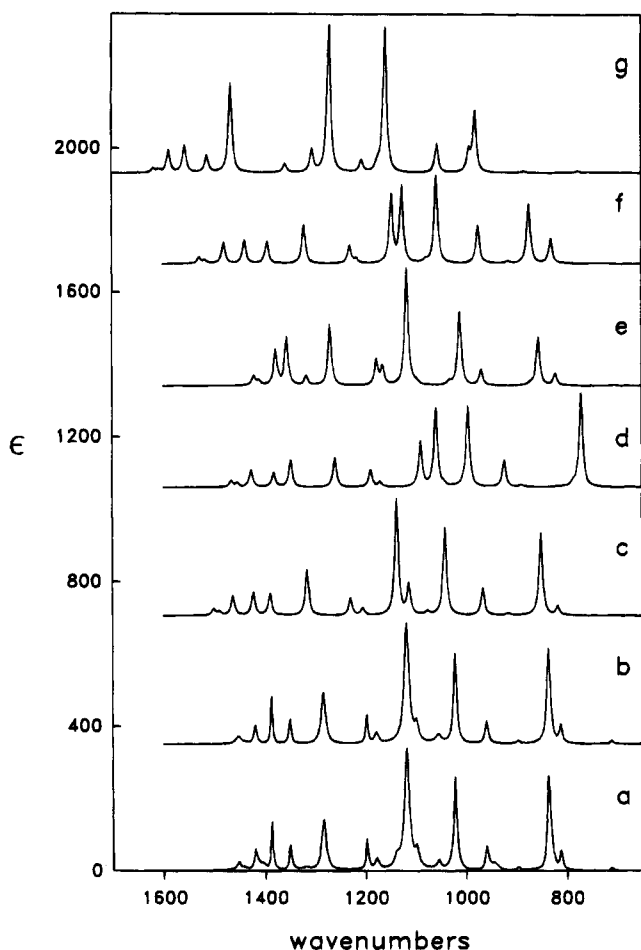
Figure 1. (a) Experimental unpolarized absorption spectra of **1** (in CCl₄ and CS₂ solutions, from ref 6). (b) Fundamental unpolarized absorption spectrum of **1**, obtained from (a) by Lorentzian fitting.[6] (c)—(g) Calculated unpolarized absorption spectrum of **1**. In (c), (d), and (e), force fields and APTs are calculated using DFT and B3LYP, BLYP, and LSDA density functionals, respectively. In (f) and (g) force fields and APTs are calculated using MP2 and SCF methodologies. All calculations use the TZ2P basis set. Lorentzian band half-widths, γ, are 4.0 cm⁻¹.

Figure 2. (a) Experimental VCD spectrum of (R)-**1** (in CCl₄ and CS₂ solutions, from ref 6). (b) Fundamental VCD spectrum of (R)-**1** obtained from (a) by Lorentzian fitting.[6] (c)—(g) Calculated VCD spectrum of (R)-**1**. (c)—(g) originate as in Figure 1. All calculations use SCF TZ2P local AATs. Lorentzian band half-widths, γ, are 4.0 cm⁻¹.

TABLE 1: Frequencies, Dipole Strengths, and Rotational Strengths of 1[a]

MP2			DFT/B3LYP			expt[b]		
ν	D	R	ν	D	R	ν	D	R
1528	14	−5	1500	13	−5	1453	25	−2
1516	8	4	1489	8	5	1441	3	3
1479	47	−11	1462	43	−11	1419	35	−9
1438	52	11	1422	51	11	1387	58	13
1394	52	27	1389	50	28	1350	40	42
1320	97	9	1316	112	3	1284	161	26
1230	47	−11	1229	44	−4	1198	47	−21
1216	14	0	1204	19	−5	1178	35	−17
1146	191	82	1137	327	99	1118	483	178
1125	219	−40	1113	87	−58	1099	51	−83
1077	10	−12	1076	11	−6	1055	40	−23
1056	271	−50	1041	268	−50	1022	251	−102
973	126	10	966	91	7	959	70	12
914	9	−29	914	8	−27	896	10	−54
873	221	33	850	310	46	836	371	78
829	97	26	817	34	10	812	55	29
714	3	−3	712	2	2	711	13	15

[a] Frequencies, ν, in cm⁻¹, dipole strengths D in 10^{-40} esu² cm², and rotational strengths R in 10^{-44} esu² cm². R values are for (R)-(+)-**1**. [b] Reference 6.

consequence in comparison.) We therefore conclude that the B3LYP, BLYP, and LSDA force fields are of significantly different accuracy, the B3LYP force field being the most accurate.

The qualitative agreement of the absorption and VCD spectra calculated using the B3LYP functional with the experimental spectra is impressive. The quantitative agreement of theory and experiment can be assessed from the calculated and experimental frequencies, dipole strengths, and rotational strengths, given in Table 1. Calculated frequencies are greater than experimental frequencies throughout, the average and maximum deviations being 25 cm⁻¹/2.0% and 48 cm⁻¹/3.3%. Some fraction of the differences in calculated and experimental frequencies can of course be attributed to anharmonicity and solvent effects. The calculated dipole strengths are in excellent qualitative agreement with experimental values; quantitative differences are attributable to a combination of residual errors in the DFT/B3LYP/TZ2P calculation, anharmonicity, solvent effects, and experimental error. Calculated rotational strengths are also in excellent qualitative agreement with experimental values. The quantitative agreement is somewhat poorer than in the case of dipole strengths. This is undoubtedly attributable to the lower accuracy of the AATs, compared to the APTs, due to the absence of correlation in the calculation of local AATs.
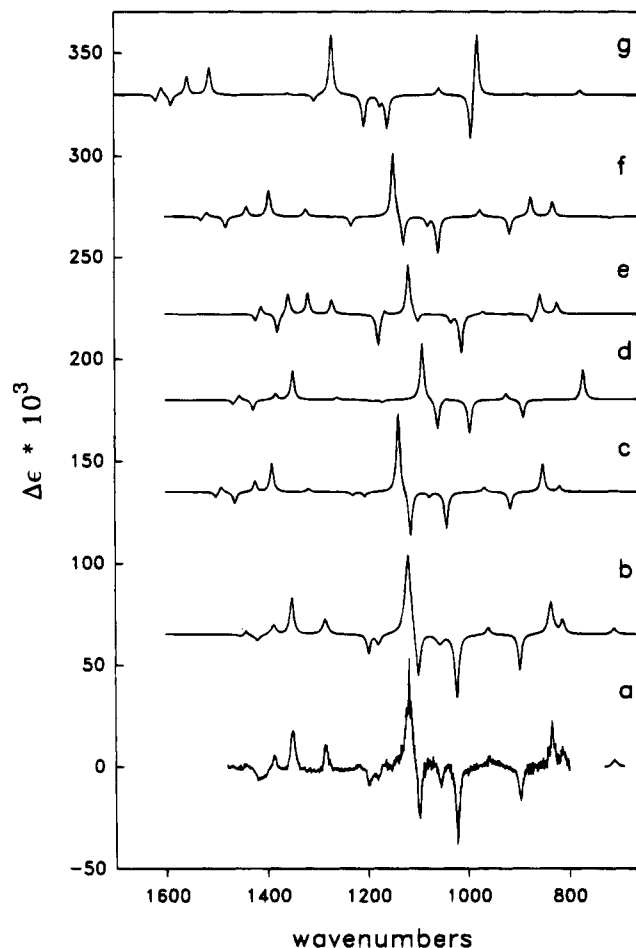
The results of TZ2P MP2 calculations[22] are also given in Table 1 and in Figures 1 and 2. The agreement with experiment of the spectra calculated using the MP2 force field is slightly worse than obtained from the B3LYP force field. The most prominent difference is in the relative absorption intensities of
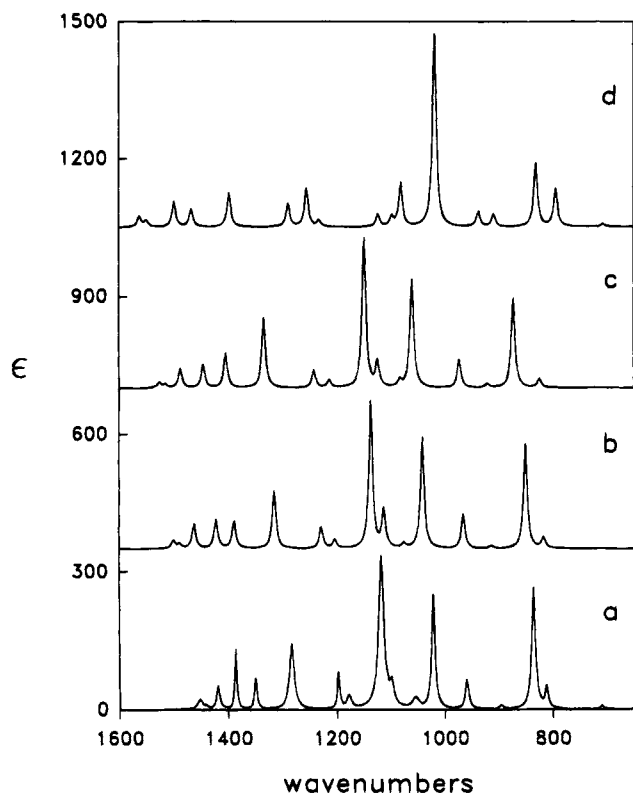
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Figure 3. (a) Fundamental unpolarized absorption spectrum of **1**, as in Figure 1b. (b)—(d) Calculated unpolarized absorption spectrum of **1**. In (b), (c), and (d) force fields and APTs are calculated using DFT, the B3LYP density functional, and respectively the TZ2P, 6-31G*, and 3-21G basis sets. Lorentzian band half-widths, γ, are 4.0 cm^{-1}.

Figure 4. (a) Fundamental VCD spectrum of (R)-**1**, as in Figure 2b. (b)—(d) Calculated VCD spectrum of (R)-**1**. (b)—(d) originate as in Figure 3. All calculations use SCF TZ2P local AATs. Lorentzian band half-widths, γ, are 4.0 cm^{-1}.

the bands calculated between 1100 and 1150 cm^{-1}. On the other hand, the agreement is significantly better than obtained from the BLYP and LSDA force fields. We conclude that the MP2 force field is respectively lower, higher, and higher in accuracy than the B3LYP, BLYP, and LSDA force fields.

The quantitative agreement of frequencies, dipole strengths, and rotational strengths calculated from the MP2 force field with experimental values can be assessed from Table 1. Calculated frequencies are in all cases greater than experimental frequencies, the average and maximum deviations being 36 cm^{-1}/3.0% and 75 cm^{-1}/5.2%. The differences are in all cases greater than for the B3LYP force field and, consequently, so are the average and maximum deviations. Calculated dipole strengths are in most cases further from experimental values than those obtained from the B3LYP force field. Comparison of both frequencies and dipole strengths thus supports the conclusion that the harmonic force field is less accurately calculated by the MP2 methodology. Rotational strengths calculated from the MP2 force field are in good qualitative agreement with both experimental values and the predictions of the B3LYP force field. Neither of the calculations exhibits clear-cut quantitative superiority.

Absorption and VCD spectra obtained from the SCF harmonic force field are also shown in Figures 1 and 2. Both absorption and VCD spectra are qualitatively different from the experimental spectra, the differences being sufficiently large that a 1-to-1 correspondence between calculated and observed bands cannot be arrived at; i.e., the predictions are insufficiently accurate to yield a convincing assignment of the experimental spectra. It is obvious that the SCF force field is drastically lower in accuracy than the DFT and MP2 force fields.

The calculations presented in Figures 1 and 2 and in Table 1 use a large basis set—TZ2P—in order to reduce basis set errors
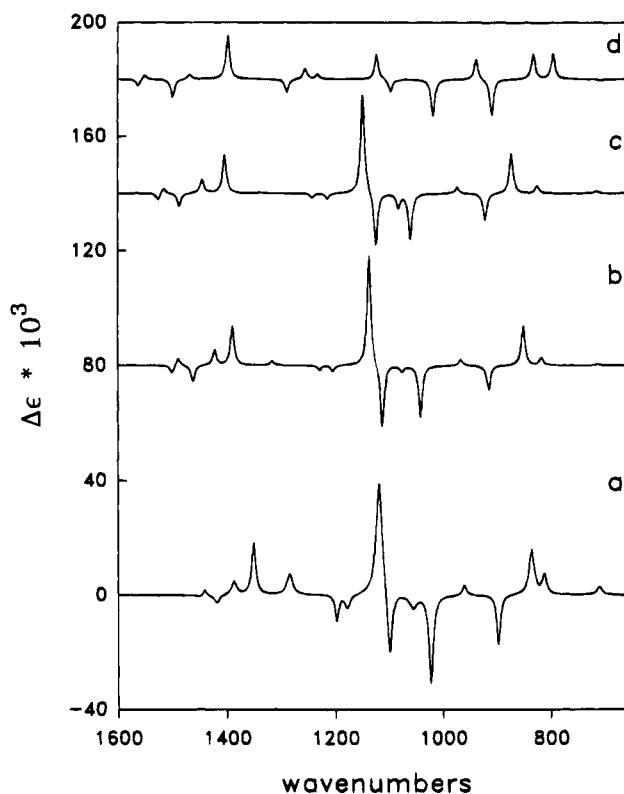
to the maximum extent. Having established the superiority of the B3LYP functional over the LSDA and BLYP functionals, it is of interest to examine the basis set dependence of the spectra predicted using the B3LYP functional. Figures 3 and 4 compare absorption and VCD spectra calculated using the 3-21G and 6-31G* basis sets to those obtained at the TZ2P level and to experiment. Local AATs are calculated at the TZ2P basis set level throughout, and the variations in spectra are due entirely to variations in the DFT force fields and APTs with basis set. The absorption and VCD spectra predicted using the 6-31G* and TZ2P basis sets are identical qualitatively and very little different quantitatively. The agreement with the experimental spectra is almost equally good. The 3-21G basis set yields spectra substantially different from those obtained using the 6-31G* and TZ2P basis sets and in much worse agreement with experiment.

Conclusion

In the case of **1**, and at the TZ2P basis set level, the DFT force field calculated using the B3LYP density functional yields mid-IR absorption and VCD spectra in impressive agreement with experiment. DFT force fields calculated using the LSDA and BLYP density functionals yield spectra of significantly lower accuracy. The MP2 and SCF force fields yield spectra slightly less and much less accurate, respectively, than the DFT/B3LYP force field. Calculations on a wide variety of molecules are clearly required to define the generality of these results. Such calculations are under way.

While the LSDA and BLYP functionals have been widely used in DFT calculations of vibrational frequencies,[2] this is not the case for hybrid functionals of the type recently introduced by Becke,[12] and their accuracy in predicting vibrational force fields was not obvious. Our results for **1** using the B3LYP functional support the conclusion that such hybrid functionals

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can lead to vibrational force fields, frequencies, and spectra, as well as thermochemical properties, of superior accuracy.

Our results also show that B3LYP calculations converge rapidly with increasing basis set size and that the cost-to-benefit ratio is optimal at the 6-31G* basis set level. 6-31G* will be the basis set of choice in B3LYP calculations on much larger molecules.

Our calculations clearly demonstrate the sensitivity of predictions of vibrational spectra to the accuracy of the force field and in the case of DFT calculations to the choice of density functional. The comparison to experimental spectra of vibrational spectra predicted from future generations of density functionals should be of significant utility in defining their relative accuracies. In the case of chiral molecules, the information content of vibrational spectroscopy is considerably enhanced when absorption and VCD spectra are utilized in combination.

VCD spectroscopy is potentially a powerful tool in elucidating the stereochemistry of chiral molecules. The work reported here clearly supports the expectation that DFT now provides a basis for calculations of VCD spectra at a useful level of accuracy for molecules much larger than **1**. This capability will be documented in forthcoming publications.

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