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Ab Initio Calculation of Vibrational Circular Dichroism Spectra Using Accurate Post-Self-Consistent-Field Force Fields: *trans*-2,3-Dideuteriooxirane

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The ab initio calculation of harmonic force fields using post-self-consistent-field (post-SCF) methods has recently increased greatly in efficiency. As a result, accurate post-SCF harmonic force fields are now achievable for experimentally accessible chiral molecules. This in turn, permits for the first time, comparison to experiment of ab initio predictions of vibrational circular dichroism (VCD) spectra based on accurate harmonic force fields. This advance is exploited here in the calculation of the VCD spectrum of trans-2,3-dideuteriooxirane using a large basis set MP2 force field. Excellent accord with recent experimental work is achieved. With the exception of C–H and C–D stretching modes, residual differences between predicted and experimental VCD intensities can be attributed to the incomplete inclusion of correlation in the calculation of atomic axial tensors.

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1. INTRODUCTION

The prediction of the vibrational circular dichroism (VCD) spectrum of a chiral molecule at the harmonic level of approximation requires the calculation of its equilibrium geometry, harmonic force field, atomic polar tensors, and atomic axial tensors [1–3]. These molecular properties are most accurately calculated using ab initio methods [4–7]. While predictions of VCD spectra based on ab initio calculations at the self-consistent-field (SCF) level of approximation have achieved substantial success in reproducing experimental spectra [8–25], they have been significantly limited by the inherent deficiencies of the SCF approximation. Accurate calculations require post-SCF methods.

Recently, the feasibility of the calculation of accurate harmonic force fields using post-SCF methods has increased sufficiently to permit their use in predicting VCD spectra of experimentally accessible chiral molecules. Consequently, it is now practicable to compare experimental VCD spectra to theoretical predictions which are not limited in accuracy by uncertainties in the harmonic force field. In turn, the origins of the remaining discrepancies between theory and experiment can be more precisely analyzed. Here we report the first calculations of VCD spectra which take advantage of this progress. Specifically, we report calculations of the VCD spectrum of trans-2,3-dideuteriooxirane (**1**) based on a harmonic force field obtained at the MP2 level of approximation using a large basis set. The results are compared to the recently published experimental VCD spectra of Freedman et al. [26] for solutions of **1**. The accuracy of the calculations is limited only by the incomplete inclusion of correlation in the calculation of atomic axial tensors and by the absence of any consideration of anharmonicity and condensed-phase effects. The magnitudes of the errors arising from the neglect of the contributions are evaluated. The analysis is assisted by comparisons of experimental vibrational frequencies and unpolarized absorption intensities for **1**, oxirane **2**, and oxirane-d_4 (**3**)—in solution for **1** [26] and in the gas phase for **2** and **3** [27–28]—to the results of calculations using the same force field and atomic polar tensors as used in predicting the VCD of **1**. There results a more sophisticated analysis of the deviations between a calculated and an experimental VCD spectrum than heretofore achievable.

2. RESULTS AND DISCUSSION

The harmonic vibrational frequencies and rotational strengths of **1**, calculated using a [8s6p3d/6s3p] basis set (hereafter referred to as VD/3P) [7], are given in Table 1. The harmonic force field and atomic polar tensors $P^{\lambda}_{\alpha\beta}$ were obtained at the MP2 level via analytical derivative techniques [29] using a

Table 1. Vibrational Frequencies, Intensities, Dipole Strengths, and Rotational Strengths of 1[a]

$\bar{\nu}$			I		D			R					
Calc		exp[b]	Calc	exp[b]	Calc		exp[b]	Calc			exp[b]	AAT CC[c]	APT CC[d]
A	B		MP2[f]		SCF[e]	MP2[f]		SCF[e]	MP2[f,g]	(P·M/P·L)			
	3,217	3,027	25.0	40.1	50.9	31.0	53	29.1	22.8	(18.6/4.2)	11.4		−6.3
3,212		3,014	6.0		7.4	7.4		−25.0	−24.4	(−20.4/−4.0)	−8.9		0.6
2,366		2,252	5.1	3.2	9.0	8.6	5.7	13.7	12.7	(9.3/3.3)	12.1		−1.0
	2,353	2,232	16.4	15.1	45.9	27.7	27	−14.1	−11.2	(−8.1/−3.1)	−10.4		2.9
1,439			3.0		12.6	8.4	(12)	−9.9	−8.3	(−8.1/−0.2)	(−15)		1.6
	1,380		0.2		1.1	0.6	(2.3)	−1.9	−1.3	(−1.2/−0.1)	(−2.5)		0.6
1,266		1,226	6.3	9.1	26.7	19.7	29.6	11.9	10.9	(12.4/−1.5)	24.1	13.2	−1.0
1,147		1,109	0.5		0.1	1.9		1.2	−6.3	(−5.4/−0.8)	−4.9	1.4	−7.5
	1,128	1,102	1.8	2.4	11.1	6.3	8.6	9.6	10.1	(2.3/7.8)	11.1	1.0	0.5
973		948	13.9	12.8	108.3	57.1	54	−36.9	−28.2	(−30.5/2.3)	−29.0	−0.8	8.7
	922	914	2.8	1.4	20.1	11.9	6.3	−1.7	−3.7	(0.9/−4.6)	−6.2	−2.5	−2.0
900			27.7		192.0	122.9		7.1	8.0	(17.0/−9.0)	(~ + 5)		0.9
	820		8.0		59.3	38.7		1.5	1.7	(0.3/1.4)	(+)		0.2
774			22.1		148.2	113.9		14.4	11.8	(6.4/5.3)			−2.6
	675		0.1		1.5	0.8		0.6	0.0	(0.1/−0.2)			−0.6

[a] Frequencies $\bar{\nu}$, in cm^{-1}; dipole strengths, D, in 10^{-40} esu^2 cm^2; intensities, I, in km/mol; rotational strengths, R, in 10^{-44} esu^2 cm^2. Rotational strengths are for the (*S*,*S*) enantiomer.

[b] From Freedman et al. [26], in C_2Cl_4 solution for C–H and C–D stretching modes and in CS_2 solution otherwise; values in parentheses estimated from gas-phase data. Rotational strengths are not normalized to 100% enantiomeric excess (ee); ee for (*S*,*S*)-1 and (*R*,*R*)-1 were estimated to be 94%.

[c] Contribution of correlation correction to local atomic axial tensors to rotational strength: R(exp) − R(MP2).

[d] Contribution of correlation correction to atomic polar tensors to rotational strength: R(MP2)–R(SCF).

[e] Calculation using SCF atomic polar tensors.

[f] Calculated using MP2 atomic polar tensors.

CRAY-2 version of GAUSSIAN 92 [30]. Atomic axial tensors, $M^{\lambda}_{\alpha\beta}$, were calculated using the distributed origin gauge [2,7,13,31,32], when

$$M^{\lambda}_{\alpha\beta} = (I^{\lambda}_{\alpha\beta})^{\lambda} + \frac{i}{4\hbar c} \sum_{\gamma\delta} \varepsilon_{\beta\gamma\delta} \, R^{0}_{\lambda\gamma} \, P^{\lambda}_{\alpha\beta} , \tag{1}$$

where $(I^{\lambda}_{\alpha\beta})^{\lambda}$ is the atomic axial tensor of atom λ evaluated with the origin at the equilibrium position of nucleus λ, $\vec{R}^{0}_{\lambda}$. The "local" atomic axial tensors, $(I^{\lambda}_{\alpha\beta})^{\lambda}$, were calculated at the SCF level via analytical derivative techniques [33,34] using a Cray Y-MP version of CADPAC 5.0 [35]. The atomic axial tensors are thus only partially corrected for correlation. The use of the distributed origin gauge guarantees origin-independent rotational strengths [2]. The VCD spectrum derived from the calculated rotational strengths and the experimental VCD spectrum of Freedman et al. [26] are shown in Figures 1 and 2 and are in obvious correspondence, permitting unambiguous assignment of all experimental features to fundamental transitions. The assignment, together with the rotational strengths obtained by Freedman et al. from the experimental VCD spectrum, is given in Table 1.

The accuracy of predicted rotational strength is a composite function of the accuracies of the harmonic force field, the atomic polar tensor and the atomic axial tensors, and, in addition, the magnitude of anharmonicity and condensed-phase contributions, which are not included in the theoretical formalism. The accuracies of the force field and atomic polar tensors and the significance of anharmonicity can be independently assessed by comparison of the frequencies and unpolarized absorption intensities predicted for the undeuterated and perdeuterated isotopomers of oxirane, oxirane (**2**) and oxirane - d_4 (**3**), with the accurate gas-phase results of Nakananga [27–28]. As seen from Table 2, excluding C–H and C–D stretching modes, calculated and observed frequencies differ by 2.2% on average; the maximum error is 3.9%. The errors for C–H and C–D stretching modes are substantially larger: 5–7% and 4–5%, respectively. Although harmonic frequencies for isotopomers of oxirane have not been derived from experimental data, the contributions of anharmonicity are known in many other small molecules [4]. By comparison with such data, it is clear that the calculated errors for **2** and **3** are comparable to anharmonicity contributions and that, with the respect of the force field, the harmonic limit has been effectively realized. In the case of intensities, excluding the C–H and C–D stretching modes, calculated

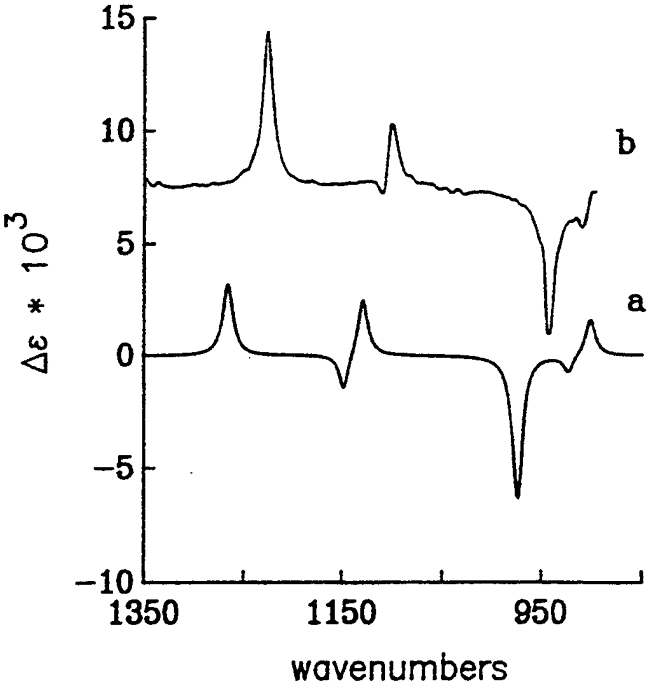

Figure 1. Predicted (a) and experimental (b) VCD spectra of 1. The predicted spectrum results from frequencies and rotational strengths are given in Table 1. Lorentzian band shapes are assumed [11,15]. The half-width at half-height (γ) is arbitrarily chosen to be 6.0 cm^{-1} for all bands [26].

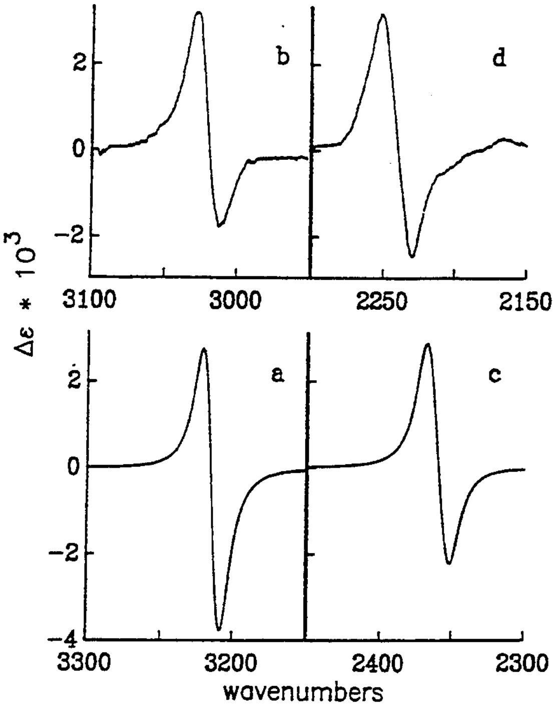

Figure 2. Predicted (a,c) and experimental (b,d) VCD spectra result from frequencies and rotational strengths given are in Table 1. Lorentzian band shapes are assumed [11,15]. The half-width at half-height (γ) is arbitrarily chosen to be 10.0 cm^{-1} for all bands [26].

and experimental intensities differ on average by 0.8 km/mol, while the quoted experimental uncertainties are on average 0.9 km/mol. Thus, calculated and experimental intensities agree within experimental error. This result confirms the excellent accuracy of the force field and of the normal coordinates derived therefrom. In addition, it demonstrates that the errors in intensities arising from errors in the calculated atomic polar tensors and from anharmonicity are both less than experimental error. Thus, with respect to intensities the harmonic limit has been effectively reached and is sufficient. In the case of the C–H and C–D stretching modes, the differences between calculated and experimental intensities are significantly larger and, in addition, are substantially greater than the experimental errors. The differences for the C–H modes are appreciably larger than for the C–D modes. In view of the excellent accuracy of the calculations for all other modes, these discrepancies can only be due to anharmonicity. Thus, for these specific modes, the harmonic limit is clearly insufficient.

Since the same force field and atomic polar tensors determine the frequencies and intensities of all isotopomers of oxirane, the frequencies and intensities of **1** should be as accurately predicted as those of **2** and **3**. Comparison to the results of Freedman et al. [26] (Table 1) supports this expectation. Excluding C–H and C–D stretching modes, the error in frequencies is 2.5% on average, the maximum error being 3.4%. The error in intensities is 1.5 km/mol on average. Although the number of modes on which these statistics are based is small, the average errors are very similar to those for **2** and **3**. Experimental uncertainties were not reported for **1**, and we cannot directly compare the differences between theory and experiment to experimental errors. In contrast to **2** and **3**, the experimental parameters for **1** are derived from spectra in solution. The comparable accuracies of predicted frequencies and intensities for **1**, **2**, and **3** lead to the conclusion that condensed-phase effects are small, i.e., that they are less than either anharmonicity effects or experimental errors, whichever are limiting.

The predicted rotational strengths of **1** are in perfect agreement with the experimental parameters derived by Freedman et al. with regard to both sign and relative magnitude (Table 1). The differences in absolute magnitudes of predicted and experimental rotation strengths could originate either in theoretical or in experimental error. Experimental uncertainties were not reported and are not easily estimated. For three bands, rotational strengths are estimates from gas-phase data. In addition, the C–H and C–D stretching rotational strengths are particularly susceptible to uncertainty since they derive from the deconvolution of unresolved, oppositely signed couplets. To a substantial degree, the differences between predicted and experimental rotational strengths are likely to be attributable to experimental uncertainties. With regard to the calculations, leaving aside the C–H and C–D stretching modes, the previous discussion

Table 2. Vibrational Frequencies and Intensities for **2** and **3**[a]

Oxirane (2)									Oxirane-d_4 (3)								
$\tilde{\nu}$					I				$\tilde{\nu}$					I			
calc				exp[b]	calc		exp[b]		calc				exp[b]	calc		exp[b]	
A_1	A_2	B_1	B_2		SCF[c]	MP2[d]			A_1	A_2	B_1	B_2		SCF[c]	MP2[d]		
			3,269	3,065	40.3	25.3	36.24	(4.69)				2,439	2,322	28.6	18.0	23.77	(3.11)
	3,255				0	0				2,432				0	0		
3,164				3,005	13.4	13.4	6.04	(3.58)	2,308				2,204	9.2	8.7	7.17	(1.44)
		3,156		2,987[e]	42.1	24.6	44.31	(5.95)[e]			2,276		2,177	25.2	14.7	19.89	(2.69)
1,555				1,497	2.2	1.5	1.04	(0.42)	1,346				1,312	9.4	6.0	6.43	(0.52)
		1,526		1,470	0.0	0.1	0.34	(0.25)			1,119		1,083	0.1	0.0	0.05	(0.11)
1,309				1,270	13.8	11.2	13.16	(0.45)	1,043				1,013	1.1	1.1	1.69	(0.78)
	1,182				0	0			980				968	46.4	22.8	23.14	(3.05)
			1,167		7.9	4.0				943				0	0		
		1,157			0.0	0.6	4.33	(0.48)			908		900	0.5	0.0	0.10	(0.14)
1,154					0.3	0.4						906	898	8.4	4.8	3.80	(0.57)
	1,061				0	0					811		812	11.1	7.5	6.76	(0.79)
890				877	101.2	66.8	63.94	(2.60)	770				752	48.8	37.6	34.23	(2.64)
			833	808	0.4	0.2	0.21	(0.21)		753				0	0		
		824		822	12.5	8.3	8.56	(0.80)				594	577	0.3	0.1	0.45	(0.30)

[a] Frequencies, $\tilde{\nu}$, in cm^{-1}; intensities, I, in km/mol.

[b] Gas-phase frequencies and intensities from Nakanaga [27–28]; quoted errors are in parentheses.

[c] Calculated using SCF atomic polar tensors.

[d] Calculated using MP2 atomic polar tensors.

[e] Corrected for Fermi resonance with (1,497 + 1,470)-cm^{-1} combination.

of unpolarized absorption intensities shows that errors in rotational strengths arising from errors in the harmonic force field and atomic polar tensors, from the neglect of anharmonicity and from the neglect of solvent effects, should be insignificant (assuming that solvent effects on VCD intensities are no longer than on unpolarized absorption intensities). There remain the errors arising from the incomplete inclusion of correlation in the atomic axial tensors—specifically, from the evaluation of the "local" atomic axial tensors $(I^{\lambda}_{\alpha\beta})^{\lambda}$ at the SCF level of approximation. If experimental errors are ignored, the magnitudes of these errors are the differences between calculated and experimental rotational strengths, given in Table 1. The uncertainties in these values are equal to the experimental uncertainties. In one case—the 1,266/1,226-cm^{-1} band—the difference is large; in all other (four) cases it is relatively small. In the case of the C–H and C–D stretching modes, as discussed previously, anharmonicity is not negligible, and experimental rotational strengths are particularly uncertain. The considerable difference between the theoretical and experimental rotational strengths for the C–H stretching modes is not surprising, therefore, while the close agreement for the C–D stretching modes is likely to be fortuitous. For these modes, the contributions of errors in atomic axial tensors to differences between experimental and calculated rotational strengths, while unlikely to be negligible, cannot yet be disentangled.

The reasonableness of the preceding analysis can be further probed in several ways. First, we can examine the "P·M" and "P·L" contributions to the rotational strengths [2,15,36] originating respectively in the first and second terms in the atomic axial tensors (equation 1). The former is subject to the correlation errors of the SCF $(I^{\lambda}_{\alpha\beta})^{\lambda}$ tensors while the second in not. Significant errors are thus to be expected only when the "P·M" term is dominant and not when the "P·L" term is dominant. The magnitudes of these two contributions are given in Table 1. In most cases, the "P·M" term is dominant. In the particular case of the 1,266/1,226-cm^{-1} mode, the only band for which the estimated correlation error was large, the "P·M" contribution is overwhelmingly dominant. Our analysis is therefore not inconsistent with the relative magnitudes of "P·M" and "P·L" contributions to the rotational strengths.

In addition, we can examine the sensitivity of rotational strengths to the exclusion of correlation in the calculation of the atomic polar tensors. VD/3P atomic polar tensors were calculated at the SCF level of approximation (using analytical derivative methods and the Cray Y-MP implementation of CADPAC 5.0) and substituted for the MP2 atomic polar tensors in calculating unpolarized absorption intensities for **1**, **2**, and **3** and rotational strengths for **1**, with the results given in Tables 1 and 2. With very few exceptions, unpolarized absorption intensities are increased, the largest increases being around a factor of 2. The rotational strengths of **1** are affected in a more complex manner, as is to be expected since changes in the atomic polar tensors affect both electric and magnetic dipole transition moments, in magnitude and in direction. In one case, the 1,147/1,109-cm^{-1} transition, the sign is changed. The magnitudes of the changes are given in Table 1 and can be seen to vary considerably. The errors in the calculated rotational strengths arising from the neglect of correlation either in atomic polar tensors or in atomic axial tensors must be comparable, since atomic polar and axial tensors are inextricably linked [7]. The values obtained by calculation in the case of the atomic polar tensors and from differences between theory and experiment for the atomic axial tensors are consistent with this expectation.

3. CONCLUSION

In predicting vibrational spectra, a harmonic force field can be defined as accurate when the residual errors in vibrational energies, wave functions, and transition moments are insignificant relative to the contributions of anharmonicity. There is no practical advantage to be gained from improvements beyond this level. Following recent developments in post-SCF methods, it is now practicable to calculate harmonic force fields of this level of accuracy for chiral molecules whose VCD spectra can be observed experimentally. We have demonstrated this advance here for the specific case of trans-2,3-dideuteriooxirane (**1**). The harmonic force field is obtained from a large basis set MP2 calculation, using semidirect analytical derivative methods. The excellent accuracy of large basis set MP2 harmonic force fields has been documented by Amos, Handy, and coworkers [37–39]. The development [29] of a semidirect implementation of the analytical derivative methodology for the calculation of MP2 harmonic force fields [37,40] permits this accuracy to be realized for oxirane and its isotopomers. The accuracy of the harmonic force field is documented by comparison of calculated and experimental gas-phase vibrational frequencies and unpolarized absorption intensities for oxirane (**2**) and oxirane-d_4 (**3**). Errors in vibrational frequencies are attributable predominantly to anharmonicity. Intensities, calculated using MP2 atomic polar tensors [41], are within experimental error with the exception of C–H and C–D stretching modes; the differences here can be attributed to anharmonicity. The harmonic force field is equally successful in accounting for the frequencies and unpolarized absorption intensities of **1** in solution, showing that solvent effects are not significant. Consequently, errors in VCD intensities predicted for **1**, with the exception of the C–H and C–D stretching modes, originate predominantly in the absence of correlation in the "local" atomic axial tensors, calculated at the SCF level of approximation. For the modes whose rotational strengths were reported, these correlation errors are of reasonable magnitude and, with one exception, small.

This work constitutes the first comparison to experimental data of a theoretical prediction of a VCD spectrum based on an accurate harmonic force field. Prior predictions of VCD spectra based on ab initio calculations at the SCF level of approximation [8–25], including those for **1** [10,12,17,36], have achieved considerable success in replicating experimental VCD spectra. However, as a result of the substantially lower accuracy of the force fields used in these calculations, a detailed analysis of the contributions of the various possible sources of error has not been possible. As demonstrated here, accessibility of an accurate harmonic force field removes a major source of error from the VCD spectra and greatly simplifies the analysis of the remaining errors. Given the rapidity with which post-SCF ab initio calculations are increasing in feasibility, the range of chiral molecules for which accurate harmonic force fields are accessible and comparable analyses of VCD intensities are possible can be expected to increase substantially in the very near future. This prospect in turn serves to emphasize the importance of additional experimental studies of small, rigid chiral molecules. Despite the efforts of several groups, the number of molecules in this category for which VCD spectra have been measured remains small. Further, it is vital for analyses of the type presented here that the definition of the quantitative accuracy of experimental rotational strengths be addressed more critically. While the measurement of VCD spectra with excellent signal-to-noise ratios at acceptable spectral resolution is now straightforward [42,43], there still remains room for considerable improvement in regard to both the control of artifactual distortions and the absolute calibration of spectra.

Our work demonstrates that the errors in rotational strengths arising from the absence of correlation in the calculation of "local" atomic axial tensors are not insignificant. Consequently, the development and implementation of post-SCF methods for the calculation of atomic axial tensors is a prerequisite to the accurate calculation of rotational strengths at the harmonic level of approximation. It is to be hoped that these will occur in the near future.

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