Vibrational Circular Dichroism in HCBrClF and DCBrClF. Calculation of the Rotational Strengths Associated with the Fundamentals and the Binary Overtones and Combinations

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Abstract: A simple model anharmonic force field has been developed for bromochlorofluoromethane by adjusting force constants to the observed wavenumbers of the fundamentals and the binary overtones and combinations of HCBrClF and DCBrClF. The electric and magnetic dipole moments were represented with a fixed partial charge (fpc) model. The force field and the fpc model were first tested by calculating the electric dipole strengths of the vibrational transitions and comparing these calculations against the experimental observations and some other calculations based on a transferred polar-tensor model for the electric dipole moment. These models were then used to calculate the rotational strengths in the circular dichroism spectra of HCBrClF and DCBrClF. The calculations suggest that it may be possible to observe circular dichroism in the binary overtone and combination transitions of these molecules. They also shed some light on the previous observations of vibrational circular dichroism in the overtone bands of camphor and other chiral molecules.

Introduction

Recently it has become apparent that there are anharmonic effects in vibrational infrared circular dichroism (CD), at least for XH-stretching modes, and consequently one expects to observe significant CD in overtone and combination transitions in the vibrational spectrum. Measurement of vibrational optical activity in overtones and combinations of camphor and other molecules by Keiderling and Stephens[1] suggests that the CD spectra of these transitions may be measured at least as easily as the fundamentals. Preliminary measurements in this laboratory on several other molecules substantiate this premise.

However, the harmonic oscillator-fixed partial charge (fpc) model[2] previously used in calculations of vibrational CD spectra predicts no rotational strength for these binary transitions and often fails to predict large enough rotational strengths for the fundamental, e.g., the CH-stretching fundamentals in tartaric acid and 2,2,2-trifluorophenylethanol.[3] In recognition of the need to extend the fpc model beyond the harmonic oscillator approximation, we showed in a companion paper[4] how the calculations of rotational strengths using the fpc model may be extended to include mechanical anharmonicity; in this paper we apply this anharmonic fpc model to the molecule bromochlorofluoromethane (HCBrClF).

There are several reasons underlying our choice of this molecule. First of all, owing to the complexity of the calculations, a complete anharmonic vibrational analysis of a large molecule such as camphor is, at present, out of the question, while HCBrClF is one of the simplest optically active molecules that have been synthesized. Secondly, a good harmonic valence force field has recently been determined by Diem and Burow.[5] Thirdly, since this molecule has been partially resolved and some circular differential Raman measurements have been made on it,[6] there is a real possibility that the results of our CD calculations may eventually be compared against experiment.

We have now determined a new force field for HCBrClF constructed by adding anharmonic (cubic and quartic) terms to the harmonic valence force field of Diem and Burow[5] and adjusting the force constants to fit their observed wavenumbers of the fundamental, overtone, and combination transitions. We believe that the inclusion of anharmonicity makes our force field more realistic than one determined entirely in the harmonic-oscillator approximation. As a test of this anharmonic force field we have compared the calculated vibrational anharmonic coefficients, $x_{ss'}$, against the experimental values determined from the spectra reported by Diem and Burow.[5] We next examined the fpc model taken for the electric dipole moment by comparing the intensities of the fundamentals calculated from this model with those calculated from a polar-tensor model described by Newton and Person,[7] using atomic polar tensors transferred from the methyl halides.[8] A partial qualitative comparison with the observed vibrational intensities[5,9] was possible; this serves as a check both on the model for the electric dipole moment and on the normal coordinates calculated from the quadratic part of the potential-energy function. We have also calculated the contributions from mechanical anharmonicity to the expected intensities and polarizations of the binary overtone and combination bands as a check on the anharmonic part of the potential-energy function. Finally, we have calculated the expected rotational strengths from the anharmonic fpc model and have shown that in many of the binary transitions the vibrational CD is no less amenable to measurement than it is in the fundamentals.

The Anharmonic Force Field

It seems clear that the intramolecular potential energy, particularly in the bond-stretching coordinates, is not well represented by a harmonic-oscillator potential function. A better approximation to the true potential function in the bond-stretching coordinate, ρ, is given by the Morse function[10]

$$V(\rho) = D_e(1 - e^{-a\rho})^2 \tag{1}$$

where D_e is the bond dissociation energy. Taking derivatives with respect to ρ, we obtain the following simple expressions for the force constants:

$$K_{\rho\rho} = \frac{1}{2!}\frac{\partial^2 V(\rho)}{\rho^2} = D_e a^2 \tag{2}$$

$$K_{\rho\rho\rho} = \frac{1}{3!}\frac{\partial^3 V(\rho)}{\partial\rho^3} = D_e a^3 = -aK_{\rho\rho} \tag{3}$$

$$K_{\rho\rho\rho\rho} = \frac{1}{4!}\frac{\partial^4 V(\rho)}{\partial\rho^4} = \frac{7}{12}D_e a^4 = \frac{7}{12}K_{\rho\rho}a^2 \tag{4}$$

where a is the Morse parameter. Thus, given the quadratic

Table I. Valence Force Constants of HCBrClF. Units Are Consistent with the Potential Energy Being Expressed in aJ, the Stretching Coordinates in Å and the Bending Coordinates in Radians

	This work	Diem and Burow[a]
f_c [b]	3.452 52	3.450 38
f_f	5.364 73	5.180 40
f_h	5.326 00	5.000 99
f_b	2.582 29	2.482 55
f_{cf}	1.426 63	1.386 60
f_{ch}	0.855 75	0.804 86
f_{cb}	1.280 98	1.334 26
f_{fh}	0.776 73	0.757 14
f_{fb}	1.350 48	1.366 10
f_{hb}	0.639 15	0.617 88
f_c^f	0.845 88	0.845 88
f_c^b	0.745 70	0.745 70
f_f^b	1.077 62	1.077 62
f_{cf}^c	0.590 60	0.590 60
f_{ch}^c	0.261 49	0.261 49
f_{fh}^f	0.517 96	0.517 96
f_{hb}^h	−0.253 75	−0.253 75
f_{cb}^b	0.256 30	0.256 30
f_{hb}^b	0.093 60	0.093 80
f_{cf}^{cb}	0.211 20	0.211 20
f_{fh}^{hb}	0.020 71	0.020 71
k_{ccc} [c]	−3.020 04	0
k_{fff}	−4.811 59	0
k_{hhh}	−4.696 12	0
k_{bbb}	−2.026 59	0
k_{cccc} [c]	3.083 94	0
k_{ffff}	5.213 87	0
k_{hhhh}	5.144 81	0
k_{bbbb}	1.930 09	0

[a] Reference 5. [b] The notation for the quadratic force constants is the same as that used by Diem and Burow in ref. 5. [c] The cubic and quartic force constants are defined according to M. Pariseau, I. Suzuki, and J. Overend, *J. Chem. Phys.*, **42**, 2335 (1965).

Table II. Wavenumbers of the Fundamentals of HCBrClF and DCBrClF (cm^{-1})

s	Obsd[a]	Calcd This work	Calcd Diem and Burow[a]	Calcd harmonic wavenumbers, ω_s (this work)
		HCBrClF		
1	3025.7	3021.4	3039.4	3134.8
2	1310.8	1308.2	1301.7	1335.8
3	1205.0	1200.8	1203.3	1222.1
4	1078.1	1070.7	1073.8	1093.9
5	787.8	787.1	795.2	799.0
6	663.8	673.8	669.7	676.9
7	426.7	427.2	425.9	430.8
8	314.5	310.3	309.8	311.7
9	225.7	222.8	225.1	223.9
		DCBrClF		
1	2264.0	2270.2	2251.1	2320.7
2	1085.0	1089.5	1088.4	1110.5
3	974.6	986.1	977.3	1000.2
4	919.2	911.5	922.5	935.7
5	749.7	741.8	743.8	748.6
6	620.7	609.4	614.0	621.2
7	425.0	424.3	422.9	427.9
8	313.3	309.5	309.2	311.1
9	224.2	222.5	224.7	223.5

[a] Reference 5.

Table III. Anharmonicity Constants, $x_{ss'}$ (cm^{-1})

Anharmonicity constant, $x_{ss'}$	Calcd	Obsd[a]
	HCBrClF	
x_{11}	−54.6	−60.6[b]
x_{22}	−11.8	−11.3
x_{23}	2.2	−5.8
x_{33}	−8.0	−10.5
x_{44}	−9.1	−11.1
x_{57}	1.8[c]	−0.2
x_{68}	1.5	−0.5
x_{77}	−0.3	−1.4
x_{78}	−0.8	−6.2
x_{79}	−0.6	−3.8
x_{88}	−1.2	−2.8
	DCBrClF	
x_{22}	−10.8	−13.0
x_{68}	11.3[c]	−2.4
x_{78}	−4.0[c]	−2.7
x_{88}	6.6[c]	−0.8

[a] Calculated from data of ref 5. [b] D. F. Burow, private communication. [c] Corrected for resonance.

force constant, $K_{\rho\rho}$, and the bond dissociation energy, we may estimate the cubic and quartic force constants in the bond-stretching coordinates. We used Diem and Burow's quadratic force constants, and bond energies from Morrison and Boyd,[11] to calculate the cubic and quartic force constants for the four stretching coordinates of HCBrClF. This anharmonic force field gave calculated wavenumbers of the fundamentals differing considerably from the observed ones since no account of anharmonicity had been taken by Diem and Burow in determining their quadratic force constants. Accordingly we carried through a least-squares adjustment of the diagonal quadratic force constants to fit all Diem and Burow's observed wavenumbers[5] for the two isotopes, HCBrClF and DCBrClF. Our final set of force constants is compared with Diem and Burow's in Table I.

Results

Vibrational Energies. The observed wavenumbers of the fundamentals are compared with the calculated harmonic wavenumbers, ω_s, and the calculated wavenumbers, ν_s, corrected for anharmonicity, in Table II. Burow's calculated harmonic wavenumbers are also given. Note that the vibrational modes are numbered in order of decreasing wavenumber for both the H and D isotopes. In our calculation we took account of resonance interactions between ω_3 and $\omega_5 + \omega_7$ in HCBrClF and between ω_4 and $\omega_6 + \omega_8$, ω_5 and $\omega_7 + \omega_8$, and ω_6 and $2\omega_8$ in DCBrClF by exact diagonalization of the appropriate submatrices. We note that the anharmonic field gives a much better fit to the CH and CD stretching fundamentals which are the most anharmonic vibrational modes. The fit to the other fundamentals is about as good as that obtained by Diem and Burow; we might have improved this fit somewhat by adjusting some of the off-diagonal quadratic force constants but chose not to do this in view of the subjective nature of such an adjustment.

In our simple model of the anharmonic force field we have not included any anharmonicity in the internal bending coordinates nor any anharmonic interaction force constants in internal coordinates. But the use of nonlinear transformations from internal-coordinate space to normal-coordinate space generates anharmonic bending force constants and anharmonic interaction force constants. From previous experience, we believe that this model gives a reasonably adequate representation of the important anharmonic force constants in normal-coordinate space. As a test of our anharmonic field, we have compared in Table III the calculated anharmonicity constants, $x_{ss'}$, with the observed data where the latter were available. The agreement with experiment is seen to be quite

Table IV. Infrared Intensities and Band Shapes for the Fundamentals of HCBrClF and DCBrClF (km/mol)

		Polar tensor model				fpc model				Obsd int		Band
			% type				% type					
		Int	A	B	C	Int	A	B	C	D&B[a]	P&L[b]	type[c]
						HCBrClF						
ν_1	3025.7	23.6	0	15	85	4.1	0	2	98	3	m	
ν_2	1310.8	12.6	0	99	1	2.7	39	61	0	38	s	
ν_3	1205.0	6.4	16	42	42	5.0	18	55	27	85	vs	
ν_4	1078.1	191.3	1	78	21	20.1	0	63	37	212	vs	PQR
ν_5	787.8	67.5	64	20	16	25.3	61	20	19	223	vs	PQR
ν_6	663.8	48.2	47	34	19	26.3	49	22	29	78	vs	(A)
ν_7	426.7	5.8	0	9	91	5.3	1	3	96	22	m	
ν_8	314.5	1.2	12	33	55	0.8	3	36	61	1	w	
ν_9	225.7	0.7	57	20	23	0.8	35	56	9			
						DCBrClF						
ν_1	2264.0	27.6	0	10	89	0.2	1	13	86			(C)
ν_2	1085.0	174.1	0	83	17	13.5	0	65	35			(B)
ν_3	974.6	40.3	39	32	29	6.6	20	42	38			(C)
ν_4	919.2	9.0	22	49	29	2.0	2	10	88			
ν_5	749.7	32.7	54	28	18	14.5	47	32	21			PQR (A)
ν_6	620.7	18.3	61	25	14	11.6	61	19	20			
ν_7	425.0	6.1	0	11	89	5.6	1	3	96			(C)
ν_8	313.3	1.2	13	30	57	0.8	3	34	63			
ν_9	224.0	0.7	57	20	23	0.8	35	56	9			

[a] The relative intensities were estimated by Burow;[14] the absolute intensities are our estimates (see text). [b] Reference 9. [c] The designations PQR are taken from Table II of ref. 5. The designations (A), (B), and (C) are our interpretation of the band contours illustrated in Figure 4 of ref 5.

Table V. Transferred Polar Tensors Used for the Calculation of the Intensities of Fundamentals of HCBrClF and DCBrClF.[a] Units Are Electrons (1 e = 4.8 × 10^{-10} esu)

$$P_x^{\mathrm{F}} = \begin{pmatrix} -0.255 & 0 & 0 \\ 0 & -0.255 & 0 \\ 0 & 0 & -0.933 \end{pmatrix} \qquad P_x^{\mathrm{Cl}} = \begin{pmatrix} -0.234 & 0 & 0 \\ 0 & -0.234 & 0 \\ 0 & 0 & -0.446 \end{pmatrix}$$

$$P_x^{\mathrm{Br}} = \begin{pmatrix} -0.215 & 0 & 0 \\ 0 & -0.215 & 0 \\ 0 & 0 & -0.299 \end{pmatrix} \qquad P_x^{\mathrm{H}} = \begin{pmatrix} -0.036 & 0 & 0.056 \\ 0 & 0.073 & 0 \\ -0.024 & 0 & -0.061 \end{pmatrix}$$

[a] Reference 7.

good for the most part, which lends support to our simplified model of the anharmonic force field.

Fundamental Intensities. We next proceeded to calculate the dipole strengths of the fundamentals of HCBrClF and DCBrClF. Although we are restricted to the fpc model in rotational strength calculations at this time,[4] we may usefully compare the dipole strength calculated from the fpc model to the results found from other models such as the polar tensor model;[7] such a comparison is made in Table IV for the fundamentals. In the fpc calculation the partial charges were determined from dipole-moment data on other molecules and are C = +0.449; H, D = +0.111; F = −0.220; Cl = −0.180; Br = −0.160[12,13] in units of electrons (= 4.8 × 10^{-10} esu). Similarly, the polar tensors used for the F, Cl, and Br atoms were transferred from the corresponding methyl halide polar tensor, CH_3X.[7] The hydrogen atom polar tensor was taken from CH_3Cl (see Table V). The polar tensor for the C atom was then determined from the requirement that the sum over atoms of each element of the polar tensor must be zero.[7]

We note first that there are some marked disagreements between the intensities calculated from the fpc model and those calculated from the polar-tensor model, especially in the case of the stretching modes. This is, we believe, a manifestation of the most serious weakness of the fpc model in that there is no allowance for charge redistribution in the stretching of a bond. If one examines the polar tensors in Table V, one finds that the values of the first two diagonal elements ($\partial p^x/\partial x$ and $\partial p^y/\partial y$) for F, Cl, and Br correspond reasonably closely with the atomic charges assumed in the fpc model, but in each case the third diagonal element ($\partial p^z/\partial z$) is much larger. The polar tensors are oriented with the z axis along the CX bond (see ref 7). Therefore the values of $\partial p^x/\partial x$ and $\partial p^y/\partial y$ are most important in determining the intensities of the modes which involve bending of the CX bond, and the value of $\partial p^z/\partial z$ is most important in determining the intensity of the modes which strongly involve the CX bond stretching coordinate. It is already established that the values of the polar tensors may be transferred to other halomethanes[8] to fit reasonably the observed intensities of the stretching fundamentals, at least within a factor of 2, and it therefore seems that the fpc model will give a low estimate of the electric dipole strength for the stretching modes. The effect of using the components of the polar tensor as the partial charges in the fpc model is considered in the Appendix.

We have also included estimates of the experimental intensities of HCBrClF in Table IV. The relative intensities were determined by Burow,[14] who measured them from his spectra. He believes that the relative intensities are no more reliable than 20–25% and, in the worst cases, may be in error by as much as 100% or more. The estimates of the absolute intensities given in Table IV were determined by us. We took the spectrum of the ν_6 band of HCBrClF, shown in Figure 4F of ref 5, replotted it on an absorbance scale, and integrated it graphically to obtain a rough value of $A_6 \sim 78$ km/mol. This value was used to scale Burow's relative intensities. Although the errors in this procedure may be considerable, it does appear that the experimental values of the intensities of the stretching fundamentals are closer to the ones given by the polar-tensor model than the ones given by the fpc model.

In the calculation of the electric dipole strengths we have

Table VI. Predicted Infrared Intensities (km/mol) and Band Shapes for Selected Binary Overtones and Combinations of HCBrClF and DCBrClF

	Polar tensor model				fpc model				Obsd intensity	
		% type				% type				
	Int	A	B	C	Int	A	B	C	D&B[a]	P&L[b]
					HCBrClF					
$2\nu_1$	0.38	0	13	87	0.08	0	2	98	0.9	
$2\nu_2$	1.46	0	18	82	0.25	0	1	99	1.0	w
$2\nu_3$	0.67	1	10	89	0.12	0	4	96	2.5	vw
$2\nu_4$	1.13	2	85	13	0.11	3	64	33	*c*	m
$2\nu_5$	0.86	11	88	1	0.08	23	76	1		w
$2\nu_6$	0.32	53	33	14	0.19	1	90	9		
$2\nu_7$	0.36	88	2	10	0.16	95	1	4	2.0	w
$2\nu_8$	2.50	58	32	10	1.25	60	19	21		m
$2\nu_9$	0.06	2	1	97	0.06	6	1	93		
$\nu_1 + \nu_2$	0.02	1	90	9	0.01	43	49	8		w
$\nu_1 + \nu_3$	0.07	2	75	23	0.01	46	25	29		w
$\nu_1 + \nu_4$	0.04	1	49	50	0.004	9	0	91		vw
$\nu_2 + \nu_3$	0.05	90	10	0	0.001	1	97	2	1.3	vw
$\nu_5 + \nu_6$	0.17	49	36	15	0.03	59	0	41		w
$\nu_5 + \nu_7$	1.87	2	4	94	1.68	21	37	42	*d*	
$\nu_6 + \nu_8$	0.97	47	39	14	0.34	66	30	4	1.7	w
$\nu_6 + \nu_9$	0.51	0	98	2	0.12	2	80	18		w
$\nu_7 + \nu_8$	1.72	85	10	5	0.65	89	6	5	4.0	m
$\nu_7 + \nu_9$	0.42	4	87	9	0.12	9	52	39		
					DCBrClF					
$2\nu_1$	0.28	0	8	92	0.005	1	2	97		
$2\nu_2$	1.37	0	3	97	0.09	3	24	73		
$2\nu_3$	0.46	0	9	91	0.01	0	1	99		
$2\nu_4$	0.54	3	2	95	0.004	47	14	39		
$2\nu_5$	0.89	13	83	4	0.11	31	69	0		
$2\nu_6$	0.81	28	48	24	0.10	47	31	22		
$2\nu_7$	0.08	7	16	77	0.04	12	21	67		
$2\nu_8$	22.30	58	24	18	15.07	58	19	23		
$2\nu_9$	0.05	3	1	96	0.05	6	1	93		
$\nu_1 + \nu_2$	0.05	0	74	26	0.001	6	85	9		
$\nu_1 + \nu_3$	0.03	15	1	84	0.001	8	32	60		
$\nu_1 + \nu_4$	0.06	6	83	11	0.000	52	4	44		
$\nu_2 + \nu_3$	2.33	0	51	49	0.06	0	99	1		

[a] Reference 5. [b] Reference 9. [c] Observed but not measured. [d] Blended with ν_3; all the intensity has been ascribed to the fundamental.

available the components of the matrix elements of the dipole-moment operator in arbitrary molecule-fixed axes and it is a simple matter to rotate these components into the principal axes of the inertia tensor. In this way we obtain the polarization of each vibrational transition, which, combined with the appropriate rotational selection rules for the asymmetric top, gives the calculated band type. In most cases the polarization of the vibrational transition does not coincide with a principal axis of the inertia tensor and we therefore expect the rotation-vibration bands to be hybrids.

In Tables IV and VI we show the percentage of A, B, and C type character calculated for each band. The equilibrium rotational constants were calculated to be 0.215, 0.068, and 0.054 cm^{-1} for the H isotope and 0.208, 0.067 and 0.053 cm^{-1} for the D isotope, so each molecule is almost a prolate symmetric top. The percentages of A, B, and C character predicted by the polar tensor and fpc calculations are in close agreement for most of the bands and we conclude that the predicted band shapes are not very sensitive to the particular intensity model chosen. Our calculated band shapes match the observed contours for five of the six bands Diem and Burow show in their paper;[5] we predict more B type character than is observed in ν_3 (ν_4 in ref 5) of DCBrClF both in the polar-tensor and fpc calculations. But ν_3 and ν_4 are both CD bending modes and since they have almost the same wavenumbers, the normal coordinates are very sensitive to the details of the force field. We believe that this particular difficulty with the normal coordinate is responsible for the failure of our model to predict the correct band contour for ν_3.

Our overall conclusion from this examination of the fundamental intensities is that the fpc model probably underestimates the magnitude of the electric dipole moment but that it gives its orientation in molecule-fixed axes almost correctly.

Overtone and Combination Intensities. The calculation of the infrared intensities of the fundamentals does not use any anharmonicity parameters except indirectly when Fermi-resonance corrections are considered. The model for the overtone and combination intensities requires values of the 165 cubic normal-coordinate force constants[4] which we calculated from the force constants in Table I. We neglected the electrical anharmonicity in the polar-tensor calculation since at this time we do not have any good estimates for the second derivatives of the dipole moment.

In Table VI we show the calculated intensities and band shapes for all the overtones and some selected combination bands. The polar-tensor model predicts larger intensities than the fpc model since, as we already noted, the latter gives low values for the first derivatives of the electric dipole moment with respect to the stretching coordinates. The estimates of the binary transition intensities would be improved if we had available good experimental values of the first derivatives of the dipole moment determined from the observed intensities. From Table VI we see that there is at least a qualitative agreement with the limited observed intensity information for the H isotope.

Circular Dichroism. The rotational strengths in the anharmonic fpc approximation were calculated from the normal-

Table VII. Rotational Strengths and Dissymmetry Factors Calculated for HCBrClF and DCBrClF

	Calcd wavenumber	R, esu^2 cm^2	$\lvert G\rvert = \lvert 4R/D\rvert$
		HCBrClF	
ν_1	3021.4	6.7×10^{-47}	4.9×10^{-7}
ν_2	1308.2	2.2×10^{-45}	1.1×10^{-5}
ν_3	1200.8	-2.1×10^{-44}	5.0×10^{-5}
ν_4	1070.7	3.2×10^{-44}	1.7×10^{-5}
ν_5	787.1	-1.6×10^{-44}	5.1×10^{-6}
ν_6	673.9	1.0×10^{-44}	2.6×10^{-6}
ν_7	427.2	-9.3×10^{-45}	7.4×10^{-6}
ν_8	310.3	3.5×10^{-45}	1.4×10^{-5}
ν_9	222.8	3.9×10^{-45}	1.1×10^{-5}
$2\nu_1$	5933.5	3.5×10^{-50}	2.7×10^{-8}
$2\nu_2$	2592.6	-2.1×10^{-47}	2.1×10^{-6}
$2\nu_3$	2390.6	4.8×10^{-47}	9.2×10^{-6}
$2\nu_4$	2123.1	-7.7×10^{-47}	1.5×10^{-5}
$2\nu_6$	1345.2	2.6×10^{-45}	1.9×10^{-4}
$2\nu_7$	853.8	6.1×10^{-47}	4.3×10^{-6}
$2\nu_8$	618.2	4.6×10^{-46}	3.6×10^{-6}
$\nu_1 + \nu_2$	4329.7	-3.3×10^{-48}	2.0×10^{-5}
$\nu_1 + \nu_3$	4217.8	-2.1×10^{-48}	8.6×10^{-6}
$\nu_2 + \nu_3$	2513.6	-2.1×10^{-47}	4.4×10^{-4}
$\nu_5 + \nu_7$	1216.1	-4.5×10^{-45}	3.8×10^{-5}
$\nu_6 + \nu_8$	985.7	1.7×10^{-46}	6.6×10^{-6}
$\nu_7 + \nu_8$	736.7	6.6×10^{-47}	1.1×10^{-6}
$\nu_7 + \nu_9$	649.3	-4.7×10^{-47}	4.1×10^{-6}
		DCBrClF	
ν_1	2270.2	1.3×10^{-46}	1.4×10^{-5}
ν_2	1089.5	-2.9×10^{-44}	2.3×10^{-5}
ν_3	986.1	5.8×10^{-44}	8.7×10^{-5}
ν_4	911.5	-9.3×10^{-45}	4.3×10^{-5}
ν_5	741.8	-1.3×10^{-44}	6.6×10^{-6}
ν_6	609.4	7.5×10^{-45}	3.9×10^{-6}
ν_7	424.3	-9.8×10^{-45}	7.5×10^{-6}
ν_8	309.5	3.5×10^{-45}	1.4×10^{-5}
ν_9	222.5	3.9×10^{-45}	1.1×10^{-5}
$2\nu_1$	4482.6	4.4×10^{-50}	3.9×10^{-7}
$2\nu_2$	2157.4	-2.6×10^{-47}	6.5×10^{-6}
$2\nu_3$	1964.4	8.1×10^{-49}	1.2×10^{-6}
$2\nu_4$	1842.2	4.1×10^{-47}	2.1×10^{-4}
$2\nu_8$	625.6	5.5×10^{-45}	3.5×10^{-6}
$\nu_1 + \nu_2$	3377.1	-4.0×10^{-49}	3.0×10^{-5}
$\nu_1 + \nu_3$	3259.0	6.8×10^{-49}	4.8×10^{-5}
$\nu_1 + \nu_4$	3193.7	-3.8×10^{-49}	7.1×10^{-5}
$\nu_2 + \nu_3$	2065.8	-6.7×10^{-47}	5.3×10^{-5}
$\nu_5 + \nu_8$	1047.6	-1.1×10^{-46}	3.2×10^{-6}
$\nu_5 + \nu_9$	958.2	2.5×10^{-45}	8.6×10^{-5}
$\nu_6 + \nu_7$	1042.1	8.3×10^{-46}	6.7×10^{-5}
$\nu_6 + \nu_8$	937.7	-1.2×10^{-44}	5.4×10^{-5}
$\nu_7 + \nu_8$	729.8	-4.6×10^{-45}	4.8×10^{-6}

coordinate force constants generated by our new force field using the expressions previously derived.[4] Since at this time we are restricted to writing the magnetic moment in the fpc model, we must also write the electric moment in the fpc model to avoid an origin-dependent rotational strength.[4] Regrettably, as we have already established, the fpc model appears to underestimate the electric dipole strengths of the intense stretching fundamentals by a factor of between 2 and 10 (see Table IV). The effect is most serious in the case of the CF-stretching mode and, since this gives the dominant contribution to the matrix element of the electric dipole moment for many of the binary overtones and combinations, these matrix elements are probably seriously underestimated in the anharmonic fpc approximation. We have at present no way of knowing how faithfully the fpc approximation models the magnetic dipole moment, but it may well give a similarly low value for that quantity. In that case our predictions of the rotational strengths may well be systematically low by as much as a factor of 10.

For this reason we also show in Table VII the calculated dissymmetry factor, $G = 4R/D$, where R is the rotational strength and D is the dipole strength in cgs units.[15] Since we used the calculated values of both R and D in deriving the G values, the systematic underestimates resulting from the use of the fpc model should partially cancel. These dissymmetry factors are important because they give an indication of the chance of experimentally observing circular dichroism in the various vibrational transitions. G values as low as about 5×10^{-6} are presently measurable above 2000 cm^{-1}. Note that, although the calculated rotational strengths of the binary transitions are considerably smaller than those of the fundamentals, the G values are often as large, if not larger. Further, many of the overtone and combination bands occur above 2000 cm^{-1} and are more amenable to experimental investigations.[16]

In the treatment presented here the rotational-strength calculation for the fundamentals gives the same result as would be obtained in the harmonic-oscillator fpc calculations used previously except in cases where anharmonic resonance is explicitly introduced. If we wish to introduce anharmonicity more directly into the calculation of rotational strengths of the fundamentals, we shall need to extend the anharmonic treatment to another order in perturbation theory as described in our companion paper.[4] In this way it would be possible to take account of anharmonic coupling between a fundamental and a binary overtone or combination and, indeed, the failure of the harmonic fpc model to satisfactorily account for the large observed rotational strengths associated with the hydrogen-stretching modes of molecules like 2,2,2-trifluorophenylethanol and tartaric acid[3] suggests that such an extension may well be necessary.

However, if we take a closer look at the CH and CD stretching fundamentals in bromochlorofluoromethane, we find that there is little evidence of resonance between the stretching fundamental and the bending overtones and combinations. In fact, including a resonance interaction in the calculations had little effect on the results. Also, the CH and CD stretching overtones are calculated to have the least optical activity of all the binary transitions. If this be true in general, it may be that the CD observed by Keiderling and Stephens at about 6000 cm^{-1} in the spectrum of camphor[1] is actually due to combinations of different CH bond stretches rather than to overtones of a single CH stretch.

Examination of the G values listed in Table VII reveals that we should expect to observe circular dichroism for several transitions, even with present experimental limitations, if the molecule could be completely resolved. However, to date, this molecule has only been resolved to an optical purity of about 10%.[14] If we accept the results of our calculation we should not expect to observe any significant infrared CD with such a sample.

To test experimentally the predictions of our model calculations we estimate that we should require about 0.5 g of optically pure material to study the fundamentals and about 5 g to study the weaker binary overtones and combinations. If this material cannot be prepared it may be possible to apply the anharmonic fpc model to some other molecule which is more readily available. At present our computer programs limit us to the consideration of molecules with no more than seven atoms,[17] although, in principle, the calculation could be extended to larger molecules if we had access to a sufficiently large computer.

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Table VIII. Infrared Intensities, Rotational Strengths, and Dissymmetry Factors Calculated for HCBrClF and DCBrClF Using $\partial p^y/\partial y$ (i) and $\partial p^z/\partial z$ (ii) for the Partial Charges

	Int, km/mol		R, esu^2 cm^2		$\lvert G\rvert = \lvert 4R/D\rvert$	
	i	ii	i	ii	i	ii
			HCBrClF			
ν_1	0.19	41.6	6.1×10^{-47}	-1.2×10^{-46}	9.8×10^{-6}	8.4×10^{-8}
ν_2	0.02	58.5	3.6×10^{-45}	2.8×10^{-44}	2.7×10^{-3}	6.3×10^{-6}
ν_3	2.2	40.5	-2.1×10^{-44}	-7.1×10^{-46}	1.1×10^{-4}	2.1×10^{-7}
ν_4	33.2	252.6	3.0×10^{-44}	-5.9×10^{-44}	9.7×10^{-6}	2.5×10^{-6}
ν_5	38.4	207.1	-1.9×10^{-44}	-8.7×10^{-44}	3.8×10^{-6}	3.3×10^{-6}
ν_6	38.0	194.1	1.4×10^{-44}	1.6×10^{-43}	2.4×10^{-6}	5.5×10^{-6}
ν_7	8.2	55.6	-1.2×10^{-44}	-1.4×10^{-43}	6.3×10^{-6}	1.0×10^{-5}
ν_8	1.3	10.4	5.8×10^{-45}	6.2×10^{-44}	1.4×10^{-5}	1.9×10^{-5}
ν_9	1.3	4.6	4.8×10^{-45}	2.8×10^{-44}	8.3×10^{-4}	1.4×10^{-5}
$2\nu_1$	0.005	0.66	4.6×10^{-50}	2.1×10^{-44}	5.3×10^{-7}	1.9×10^{-8}
$2\nu_2$	0.01	2.51	7.4×10^{-49}	4.3×10^{-46}	1.3×10^{-6}	4.4×10^{-6}
$2\nu_3$	0.008	1.33	2.8×10^{-47}	-3.9×10^{-46}	8.9×10^{-5}	7.1×10^{-6}
$2\nu_4$	0.18	1.50	-7.0×10^{-47}	1.5×10^{-46}	8.0×10^{-6}	2.1×10^{-6}
$2\nu_6$	0.13	4.36	2.5×10^{-45}	-1.3×10^{-45}	2.7×10^{-4}	4.1×10^{-6}
$2\nu_7$	0.16	0.70	5.4×10^{-47}	-1.9×10^{-47}	2.9×10^{-6}	2.3×10^{-6}
$2\nu_8$	1.16	6.17	5.8×10^{-46}	5.5×10^{-45}	3.1×10^{-6}	5.6×10^{-6}
$\nu_1 + \nu_2$	0.0002	0.10	-5.4×10^{-49}	6.0×10^{-47}	1.2×10^{-4}	2.6×10^{-5}
$\nu_1 + \nu_3$	0.0003	0.13	6.5×10^{-50}	-1.1×10^{-46}	9.9×10^{-6}	3.7×10^{-5}
$\nu_2 + \nu_3$	0.001	0.10	-2.2×10^{-47}	5.3×10^{-47}	4.2×10^{-4}	1.3×10^{-5}
$\nu_5 + \nu_7$	0.97	8.99	-4.1×10^{-45}	5.2×10^{-45}	5.2×10^{-5}	7.1×10^{-6}
$\nu_6 + \nu_8$	0.31	1.20	2.2×10^{-46}	7.9×10^{-46}	6.9×10^{-6}	6.5×10^{-6}
$\nu_7 + \nu_8$	0.69	3.80	3.6×10^{-47}	-1.2×10^{-45}	3.9×10^{-7}	2.3×10^{-6}
$\nu_7 + \nu_9$	0.12	.71	-4.6×10^{-47}	1.8×10^{-46}	2.6×10^{-6}	1.6×10^{-6}
			DCBrClF			
ν_1	1.0	63.5	1.2×10^{-46}	-1.4×10^{-46}	2.7×10^{-6}	5.2×10^{-8}
ν_2	27.1	253.3	-2.7×10^{-44}	2.5×10^{-44}	1.1×10^{-5}	1.1×10^{-6}
ν_3	12.7	138.5	5.7×10^{-44}	-2.4×10^{-44}	4.5×10^{-5}	1.8×10^{-6}
ν_4	3.0	40.0	-9.6×10^{-45}	-7.8×10^{-45}	3.0×10^{-5}	1.8×10^{-6}
ν_5	19.8	87.7	-1.5×10^{-44}	-6.3×10^{-44}	5.5×10^{-6}	5.3×10^{-6}
ν_6	15.4	69.5	9.2×10^{-45}	8.7×10^{-44}	3.7×10^{-6}	7.6×10^{-6}
ν_7	8.5	57.5	-1.3×10^{-44}	-1.4×10^{-43}	6.4×10^{-6}	1.0×10^{-5}
ν_8	1.3	10.3	5.8×10^{-45}	6.3×10^{-44}	1.4×10^{-5}	1.9×10^{-5}
ν_9	1.3	4.5	4.8×10^{-45}	2.9×10^{-44}	8.3×10^{-6}	1.4×10^{-5}
$2\nu_1$	0.007	0.65	7.3×10^{-50}	6.5×10^{-49}	4.8×10^{-7}	4.5×10^{-8}
$2\nu_2$	0.10	4.83	-1.1×10^{-47}	3.7×10^{-46}	2.6×10^{-6}	1.7×10^{-6}
$2\nu_3$	0.009	1.09	7.3×10^{-48}	1.3×10^{-46}	1.5×10^{-5}	2.3×10^{-6}
$2\nu_4$	0.03	1.47	3.0×10^{-47}	-2.6×10^{-46}	1.7×10^{-5}	3.3×10^{-6}
$2\nu_8$	12.71	55.36	6.8×10^{-45}	6.8×10^{-44}	3.4×10^{-6}	7.7×10^{-6}
$\nu_1 + \nu_2$	0.003	0.08	1.6×10^{-48}	-3.0×10^{-48}	1.8×10^{-5}	1.3×10^{-6}
$\nu_1 + \nu_3$	0.002	0.12	1.0×10^{-48}	1.4×10^{-46}	1.7×10^{-5}	4.0×10^{-5}
$\nu_1 + \nu_4$	0.003	0.11	-3.5×10^{-48}	-1.4×10^{-46}	3.9×10^{-5}	4.2×10^{-5}
$\nu_2 + \nu_3$	0.17	3.18	-4.0×10^{-47}	4.8×10^{-46}	4.8×10^{-6}	3.1×10^{-6}
$\nu_5 + \nu_8$	0.57	4.20	-1.6×10^{-46}	-9.5×10^{-46}	3.0×10^{-6}	2.4×10^{-6}
$\nu_5 + \nu_9$	0.28	2.66	2.5×10^{-45}	-1.6×10^{-46}	8.5×10^{-5}	5.9×10^{-7}
$\nu_6 + \nu_7$	0.29	3.26	7.9×10^{-46}	-2.4×10^{-46}	2.9×10^{-5}	7.9×10^{-7}
$\nu_6 + \nu_8$	3.62	44.72	-1.3×10^{-44}	-6.9×10^{-45}	3.4×10^{-5}	1.5×10^{-6}
$\nu_7 + \nu_8$	9.75	44.55	-5.4×10^{-45}	-3.0×10^{-44}	4.0×10^{-6}	5.0×10^{-6}

Appendix

It was noted in the text that the fpc model calculation yielded low estimates of the electric dipole strength for the stretching modes. This is because the partial charges used in the fpc calculation are much too low to correspond with the value of $\partial p^z/\partial z$ used in the polar tensor which is most important in determining the intensities of the stretching modes. They do, however, almost match the values of $\partial p^x/\partial x$ and $\partial p^y/\partial y$ in the polar tensors which are most important in determining the intensities of modes involving the CX bond bending coordinates. Since the partial charges may, in principle, be treated as adjustable parameters, it is interesting to explore the effect of modifying the partial charges in the fpc model on the infrared intensities and rotational strengths.

We first use the $\partial p^y/\partial y$ (i) and then the $\partial p^z/\partial z$ values (ii) from the polar tensors in Table V for the partial charges, and find that we get very different results. The intensities and rotational strengths calculated for these two cases are listed in Table VIII. The results for case (i) are essentially the same as were obtained using the original estimates of the partial charges, cf. Tables IV, VI, and VII. However, if we use the diagonal z components of the polar tensors (ii) for the partial charges, we find a considerable change in the calculated intensities and rotational strengths. As might have been anticipated, the agreement between the fpc model calculation and experiment for the CF and CCl fundamental stretching intensities has been greatly improved by this adjustment of the partial charges. Although the CH-stretching fundamental and some of the bending mode intensities are now too high, there seems to have been an overall improvement in the agreement with experiment. It is likely that further refinement in the partial charges would result in an even better fit, but in view of the uncertainties in the experimental intensities, this was not deemed worthwhile.

Examination of the rotational strengths listed in Table VIII shows that the choice of partial charges can have a drastic effect on both the sign and magnitude of the calculated rotational strengths. Since the G values sometimes differ between the two cases by as much as an order of magnitude or more, it appears that refined partial charges are needed before anything more than a qualitative estimation of the measurability of the CD spectrum can be made within the fpc model.

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(16) This limit of about 2000 cm^{-1} arises through the need to employ fast detectors with a high signal to noise ratio. Most of our own measurements to date have been made with a photovoltaic InSb detector which has a 5.5-μ cutoff. The problems with signal to noise ratio are more difficult at longer wavelengths and it is doubtful that a G value less than 10^{-4} could be measured at this time.

(17) The calculation for a seven-atom molecule requires a computer with a core memory of 145K, 64-bit words.

Heavy Atom Effects on the Triplet Lifetimes of Naphthalene and Phenanthrene

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Abstract: Heavy atom effects on triplet decay rates are reported for the eight monohalonaphthalenes and for ten monohalophenanthrenes. The decrease in the lifetime with substitution is shown to vary with the square of the atomic spin-orbit coupling factor for the attached halogen. The position dependence is qualitatively related to the unpaired spin density distribution in the molecule. Investigation of the lifetimes of several polyhalogenated naphthalenes and phenanthrenes indicate both positive and negative deviations from an additive model for heavy atom effects. Substituent-induced shifts of the 0-0 band of the phosphorescence spectra are also tabulated.

It was first noted by McClure[1] in 1949 that substitution of a halogen atom for a proton in aromatic molecules has a dramatic effect on the triplet state properties. The explanation involved an enhancement of spin-forbidden processes due to an increase in spin-orbit coupling induced by the halogen atom substituent. In aromatic hydrocarbons the so-called "internal heavy atom effects" include the following: (1) the phosphorescence lifetime decreases;[1-7] (2) the fluorescence lifetime usually decreases;[2,6-8] (3) the phosphorescence quantum yield may increase;[2,7,8] (4) the intersystem crossing rate increases;[2,7,8] (5) the oscillator strength of the $T_1 \leftarrow S_0$ absorption increases;[3,9,10] (6) S_1 and T_1 are lowered in energy, i.e., the emission spectra are red shifted;[2,9-15] (7) the vibronic substructure of the absorption and emission spectra changes.[9-13]

The magnitudes of these effects are related to the nuclear charge of the substituent, and increase through the series F, Cl, Br, I. They are also dependent, in general, on the position of substitution. The present work is concerned chiefly with the first effect noted above. Other of the effects will be noted or discussed briefly.

Previous studies of the heavy atom effect on phosphorescence lifetimes suffer from two inadequacies. First, although the nuclear charge dependence for naphthalene has been quite extensively studied, investigations of other aromatic hydrocarbons have been few and incomplete. Second, a position dependence of the heavy atom effect has not been characterized or discussed in detail. Naphthalene phosphorescence lifetimes,[1] within the precision of earlier measurements, show little or no position dependence, a presumably accidental situation. Furthermore, the scatter of experimental values from different research groups[1-3] obscures any possible small position effect in naphthalene. Position effects on triplet lifetimes of other molecules have been reported by Zanker[4] and Masetti et al.[6,7] but the data are incomplete.

It was, therefore, felt that a comprehensive position and mass dependence study on a molecule other than naphthalene was in order. Phenanthrene is ideal for several reasons. First, it is a relatively simple and well-characterized aromatic hydrocarbon. In addition, it has five inequivalent substitution sites while naphthalene has only two. Furthermore, many halogenated phenanthrenes were available from a previous study of position-dependent deuterium effects.[16] In the course of the phenanthrene studies, apparent steric effects in some dihalo compounds led to an examination of some dihalonaphthalenes and a reexamination of the lifetimes of the monohalonaphthalenes.

The numbering systems for naphthalene and phenanthrene are as follows: