of those in Figure 1. The observed rotational strength is -2×10^{-45} esu^2 cm^2; the dipole strength is 1.0×10^{-39} esu^2 cm^2. The C*–H stretch, which is shown by the calculations[1] to enjoy a larger rotational strength, is difficult to study experimentally because of overlapping neopentyl C–H stretching modes.

The observed CD peaks shown in Figure 1 correspond to measured absorbance differences (base 10) of 2×10^{-5}. We checked for false peaks of this magnitude by three methods: (a) absorption base lines;[8] (b) racemic sample; (c) optically inactive molecules in an optically active solvent. No spurious CD was observed.

The present study has concentrated on C*–H and C*–D stretching modes of I and II because these are instrumentally favorable. We are now extending our experiments with these molecules to lower energies. A theoretical analysis of the structural sources of the observed vibrational CD is presented in our accompanying communication.[1]

Acknowledgment. We thank the National Science Foundation for its support *via* Grants GP-8566 and GP-27448, the University of Minnesota for a generous grant of computer time, and the National Institutes of Health for a Research Career Development Award to G. H. We are also grateful to Dr. Ilan Chabay, Mr. Bud Gibson, and Mr. Thomas Nunamaker for their contributions to the construction of the instrument.

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Received September 18, 1973

Infrared Circular Dichroism of Carbon–Hydrogen and Carbon–Deuterium Stretching Modes. Calculations

Sir:

In our accompanying communication[1] we reported measurements of the circular dichroism (CD) associated with the C*–H stretch in (*S*)-(+)- and (*R*)-(−)-2,2,2-trifluoro-1-phenylethanol (I), and the C*–D stretch in (*R*)-(−)-neopentyl-*1-d*-chloride (II). Since these data represent the first observations of Cotton effects arising from molecular vibrations in the liquid state, it is of some current interest to inquire more fully into the molecular motions responsible for the optical activity. Accordingly, we have performed normal coordinate analyses for the molecules in question and calculated the vibrational rotational strengths for the pertinent Cotton effects.

The general equations employed for calculating the vibrational rotational strength R and the vibrational dipole strength D are essentially those given by Schellman[2] for the fixed atomic charge model but multiplied by a factor[3] of $(1/2\pi)$. The charges were initially chosen by a method described previously[4] so as to reproduce the bond dipole moments listed by Smith.[5] These charges were then scaled upward (factor of 1.6 for the C*–H moment in I, factor of 1.5 for the C*–D moment in II) so as to approximate the experimental D values obtained from the absorption spectra. These final charges were then used for computing the R values. Figure 1 shows the final charges (units of $e = 4.8 \times 10^{-10}$ esu) and the geometrical data employed.

The normal coordinate calculations were carried out in the manner described by Gwinn[6] and utilized a valence force field. In the case of I, the field consisted only of diagonal force constants chosen from standard references.[7–9] To keep the calculation of manageable size, the phenyl and CF_3 groups were treated as pseudoatoms of mass 28.0 and 24.0 amu, respectively. These values were chosen so as to put the C–C stretching modes near 900 cm^{-1}, the approximate frequency of a C–C stretch.[10] The final results for I are given in Table I for the staggered conformation shown in Figure 1, along with the experimental values. To test, in part, the effects of the pseudoatom approximation, a more elaborate calculation was performed in which the pseudoatom approximation for CF_3 was relaxed. This produced no qualitative changes in the optical activity associated with the C*–H stretching mode.

Table I. Rotational and Dipole Strengths for (*S*)-(+)-2,2,2-Trifluoro-1-phenylethanol

	$\bar{\nu}$ (cm^{-1})	R (esu cm)^2	D (esu cm)^2
Obsd	2910	2×10^{-44}	1.4×10^{-39}
Calcd	2936	2.5×10^{-45}	1.5×10^{-39}

The calculations show that the R value for the 2900-cm^{-1} C*–H transition arises principally from the mixing of a small amount of the C–O–H angle bend (large magnetic dipole transition moment) with the C*–H stretching mode (large electric dipole transition moment). The mixing and the sign and magnitude of the resultant R value depend strongly on the position of the O–H bond relative to the C*–H bond. This interpretation is unaffected by modest changes in the diagonal force constants or by the introduction of off-diagonal force constants that connect motions in the C–O–H moiety to motions in the rest of the molecule. For example,

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(2) J. A. Schellman, *J. Chem. Phys.*, **58**, 2882 (1973).
(3) Using a matrix formalism, we have also derived the equations pertinent to the fixed atomic charge model. Our final expressions for R and D are entirely equivalent to those published by Schellman except for a constant multiplicative factor of $(1/2\pi)$. Schellman (private communication) informs us that the missing factor of $(1/2\pi)$ is just the result of a typographical error, and that his calculations published in ref 2 actually include the $(1/2\pi)$.
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(9) A detailed listing of all the force constants used in the calculations described in this work for I and II and the resultant frequency assignments is available from the authors upon request.
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if the appropriate force constants from the valence force field for methanol reported by Margottin-Maclou[11] are transferred, then the qualitative results of our calculations are retained. Finally, the conformational dependence of R provides a ready explanation for the observed discrepancy of 20 cm^{-1} between the CD and absorption maxima, namely, that the CD band is a population weighted sum of conformer contributions.

The calculations for II were done twice with two different force fields. For both fields the diagonal force constants for the *tert*-butyl groups were transferred from the alkane force field of Schachtschneider and Snyder[12] (S–S). However, the diagonal and off-diagonal force constants for the CHDCl end of the molecule were taken in the first instance from the alkyl chloride field of (S–S)[13] and in the second instance from the ethyl chloride field of Dempster and Zerbi[14] (D–Z). The resultant two fields will be denoted, respectively, as the (S–S)-(S–S) field and the (S–S)-(D–Z) field.

As shown in Table II, the two fields give somewhat

Table II. Rotational and Dipole Strengths for (R)-(−)-Neopentyl-*1-d*-Chloride

	Force field	$\bar{\nu}$ (cm^{-1})	R (esu cm)^2	D (esu cm)^2
Obsd		2204	-2×10^{-45}	1.0×10^{-39}
Calcd	(S–S)-(S–S)	2202	-4.0×10^{-46}	1.2×10^{-39}
	(S–S)-(D–Z)	2204	-1.0×10^{-45}	1.2×10^{-39}

different results, with the (S–S)-(D–Z) field predicting an R value more nearly in accord with experiment. This, despite the fact that the two fields predict frequencies for the C*–D stretching mode that differ by only 2 cm^{-1}. The superiority of the (D–Z) ethyl chloride field for the present purposes is probably related to the fact that it was fit to several *deuterated* isomers of ethyl chloride, while the (S–S) alkyl chloride field was fit to a series of *undeuterated n*-alkyl chlorides. However, the important inferences to be drawn are: (1) the sensitivity of the calculated R values to the precise choice of force constants when dealing with relatively small rotational strengths (*cf.* the R values for I and II) and (2) the potential utility of vibrational optical activity data as additional criteria in the selection and determination of vibrational force constants.

Some further conclusions can be tentatively drawn from the above results. First, within limits, the point charge model can probably be used in a semiempirical way to make reasonable estimates of vibrational electric dipole transition moments. However, as the calculated R values are low, by an order of magnitude in the case of I, it seems that the model may fail as regards magnetic dipole transition moments. This is in accord with the discussion of Schellman,[2] who anticipated possible underestimation of magnetic dipole transition moments by the point charge model.

Acknowledgment. We wish to thank the University of Minnesota Computer Center for a generous grant of computer time, the National Science Foundation for its

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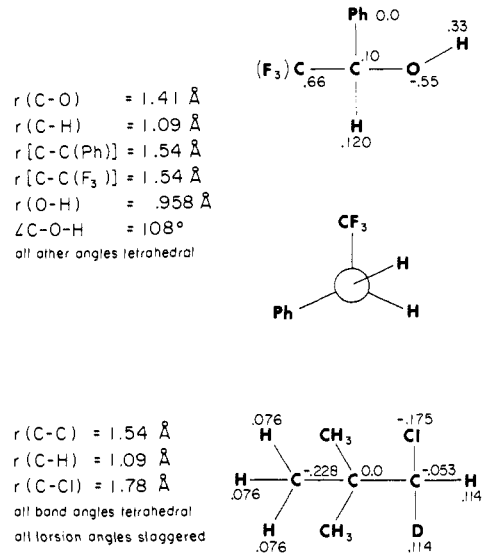

Figure 1. Molecular geometries and atomic charges (units of e = 4.80×10^{-10} esu).

support *via* Grants GP-8566 and GP-27448, and the National Institutes of Health for a Research Career Development Award to G. H.

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MINDO/3 Study of the Electronic States of Methylene[1]

Sir:

While the ground state of methylene is known[2] to be a triplet, the separation of this from the lowest singlet has been a matter of controversy. Earlier calculations[3–9] had led to values in the range 25–40 kcal/mol, in agreement with an admittedly uncertain estimate (38 kcal/mol) from electron impact work.[10] On the

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