

CCA-1813

YU ISSN 0011-1643

UDC 543.42

Original Scientific Paper

Coupled Calculations of Vibrational Frequencies and Intensities. X. Calculation of Frequencies and Infrared and Raman Activities of Large Molecules*

*Bernhard Schrader**Institut für Physikalische und Theoretische Chemie, Universität Essen,
D-4300 Essen, FR Germany*

Received January 18, 1988

The program package SPSIM can help organic chemists to make better use of the information about the structure of large molecules coded in vibrational spectra. The program is written in FORTRAN 77. SPSIM cannot exactly reproduce experimental spectra, it is rather a tool revealing the changes in the spectra when the topology, geometry or bond distribution of a molecule are changing; in addition to the frequencies for each vibration, SPSIM calculates the 'activity measure' (AM) of each component of the dipole moment vector and the polarizability tensor, the relative AMs of the bands in the infrared and the Raman spectrum together with AM based depolarization factors. AMs are zero for forbidden vibrations and, when they are large, the respective observed intensities are not usually small. The calculation of AMs takes, even for large molecules only a few seconds of CPU time. As examples results are shown for stilbene, rotational isomers of dinaphthylethylene and conformational isomers of a flexible peptide.

1. INTRODUCTION

Infrared and Raman spectra contain information on every aspect of molecular structure. The technique of infrared and Raman spectroscopy, especially its application for qualitative and quantitative analyses, has improved considerably during the last decades especially due to the introduction of computer-coupled spectrometers. However, the theoretical tools for the evaluation of the relations between the spectra and the structure of 'real life' molecules have not been improved.

There are many structural problems in organic chemistry that cannot be solved by the X-ray method but may be solved by infrared and Raman spectroscopy: equilibria of conformers or tautomers, reaction intermediates and matrix-isolated unstable molecules. The well known tables of characteristic frequencies are usually of little help. However, model calculations can help interpret the structural information coded in the spectra, especially for evaluating the changes in the spectra which accompany structural changes.

* For no. IX. of this series see reference 25.

After the work of Schachtschneider and Snyder¹, McKean and Duncan², Califano³, and especially Shimanouchi⁴, there have been few other significant developments in this field. Zerbi and Gussoni calculated the spectra of macromolecules using the so-called electrooptical parameters⁵. Gribov has applied these parameters to many organic molecules⁶. Spiekermann, Bougeard, Oelichmann, Fischer and Schrader⁷ have combined frequency-calculations with semi-empirical quantum-mechanical calculations (CNDO and MNDO) for simulation of the infrared and Raman spectra of medium-size molecules. Such methods were applied to reveal the relations between the spectra and the conformations of dienes⁸ and enones.⁹ Unfortunately this method is — due to the necessary CPU time for intensity calculation — restricted to smaller molecules with fewer than about 20 atoms.

Organic chemists have learned to carry out structure studies by simulation of NMR and ESR spectra but comparable studies with IR or Raman spectra are very rare as there is no equivalent generally applicable tool available to deal with the wealth of structural information coded in the vibrational spectra of large molecules. There are several reasons for this situation. Normal coordinate calculations of large molecules are very time consuming. Many different force fields can be considered but for large molecules the number of adjustable parameters is much larger than the number of observed frequencies. Although force constants can be calculated by quantum mechanical methods this is justifiable only for small molecules (*ab-initio* methods for less than about 10 atoms, semi-empirical methods for less than about 20 atoms).

Frequency calculations of large molecules seem to be practicable only when simplified general valence force fields are employed, but usually even then there are many considerably different sets of force constants which reproduce a given spectrum and there is no simple indication as to which is really physically representative. As Califano¹¹ has commented 'An infinite number of approximate solutions, all capable of reproducing the vibrational frequencies within a given range of error, exist for each molecule and none of them is in principle preferable to the others. Most of the physical meaning of force constants is thus lost and they assume essentially the role of spectroscopic parameters which translate into a mechanical language the vibrational information contained in the infrared and Raman spectra'.

Consequently force fields have been developed, which are so simplified that only unique solutions are found, but they yield only a crude match of the observed frequencies. For example, Cyvin has developed a force field for condensed aromatic hydrocarbons which uses only 5 force constants for the in-plane and another 5 for the out-of-plane vibrations¹². In the present paper Cyvin's force field with some additional force constants for the ethylenic system is used as an example and applied to diphenylethene (stilbene) and di- β -naphthylethene.

Arguments similar to those regarding frequencies also apply to the reproduction of intensities. Understanding of intensity changes of model molecules with the change of molecular structure would also considerably help to extract information from the observed spectra. The situation regarding intensities has been reviewed by Person and Zerbi¹³. *Ab-initio* calculations of intensities are only practicable for small molecules, and semi-empirical quantum-mechanical calculations can only be applied to small and medium-size molecules.

Methods using the so called electrooptical parameters are applicable only to classes of molecules for which these parameters have already been derived. The number of adjustable parameters is too high for this approach as to be simply applicable to large classes of different molecules. The same arguments are true regarding the so called polar tensors¹³ as a basis for intensity simulations.

For these reasons the simplified concept of activity measure (AM) has been introduced¹⁴. It is used — with some improvements — as a part of the present program package. Only seconds of computer time are necessary for the calculation of all AMs of a large molecule. As for the intensities the AMs for forbidden vibrations are zero and for the allowed ones they are non-zero. If the very few necessary parameters are chosen properly, large AMs are usually found for vibrations which are strong in the observed spectra.

This paper presents SPSIM, a program package which allows model calculations of the vibrational spectra of large organic molecules by the application of simplified force fields together with the AMs.

2. THE PACKAGE SPSIM

The structure of the package SPSIM is shown in Figure 1. From bond lengths and angles and the atomic masses as input LIM calculates the Cartesian coordinates of the atoms with respect to the axes of the inertial ellipsoid and with the centre of gravity as origin.

The following programs, AXS and CAR, are modified programs published originally by Shimanouchi in 1968¹⁵. AXS needs as input definitions of the internal coordinates and of the force constants and prepares the so called AXSM-matrix.

CAR needs as input the AXSM-matrix and the values of the force constants, it determines the frequencies and the eigenvectors in Cartesian coordinates, the Jacobi-matrix and the potential energy distribution (PED), both in terms of the force constants.

ACT transforms the eigenvectors into activity measures (AMs). The procedure has been described in¹⁴. Alternatively other programs for intensity calculations, which use the Cartesian coordinates, the atomic numbers and eigenvectors as input can be used here, applying the extended Hückel (AEH), MNDO or CNDO (AMN, ACN) or *ab initio* (ABI) procedures.

Firstly for each vibration the Cartesian coordinates of the atoms for +Q and -Q, the extrema of the vibrational motion, are calculated (Figure 2)⁷.

Secondly for the calculation of the infrared activity measure (IR-AM) a relative charge has to be put on each atom. By summing the products of the Cartesian coordinates of the atoms *i* with its charges, the components of the molecular dipole moment are calculated. Its difference for +Q and -Q gives the components of the IR-AM (equation 1). Treated like $(\partial\mu/\partial Q)$ using standard equations^{16,17}

$$\left(\frac{\partial\mu_x}{\partial Q}\right) \sim \sum_i x_i^{+Q} q_i - \sum_i x_i^{-Q} q_i \quad (1)$$

it yields the AMs instead of intensities. The AMs represent that part of the infrared intensity which is given by the shift of atomic charges. It does not,

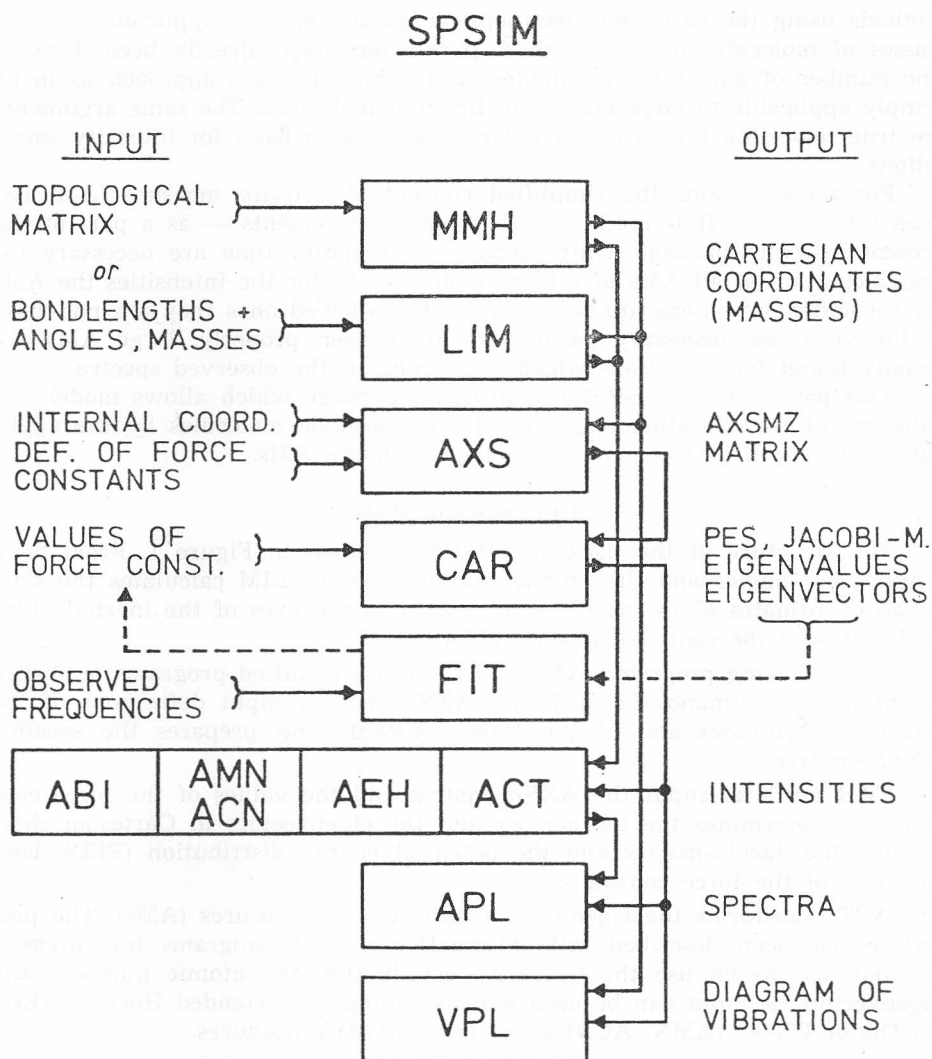


Figure 1.

however, take into account the changes of the dipole moment as a result of the rehybridization due to the changes of the intermolecular distances and angles. Therefore, a large value of the IR—AM is not strictly related to a strong infrared band and vice versa. However, if the IR—AM is exactly zero, the vibration is usually forbidden in the infrared.

Thirdly for the calculation of the Raman activity measure (RA—AM) the Cartesian coordinates of the atoms for $+Q$ and $-Q$ are needed. They have to be defined with the centre of mass of the molecule as origin. Now the sum of the products of two Cartesian coordinates of each atom with an 'atomic

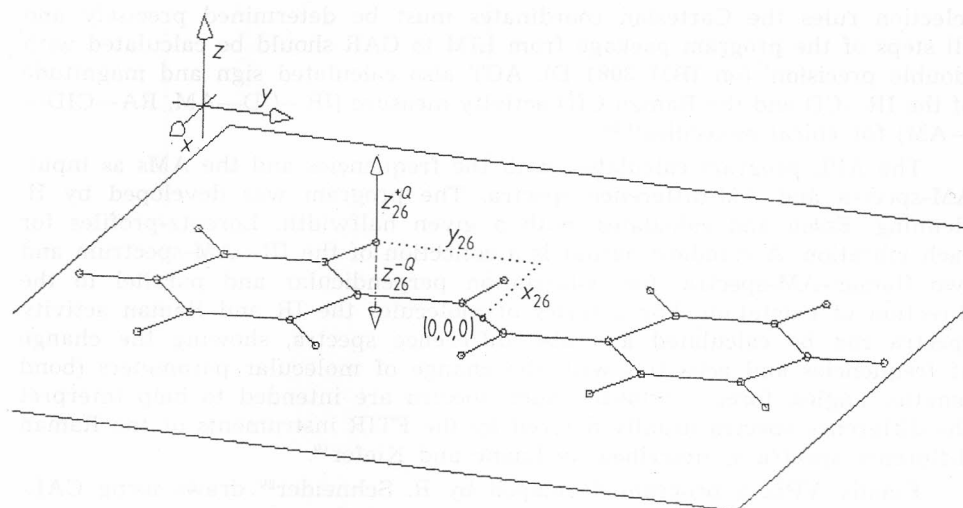


Figure 2.

radius' r_i is calculated. Its difference for $+Q$ and $-Q$ gives the components of the RA-AM (equation 2)

$$\left(\frac{\partial \alpha_{xy}}{\partial Q}\right) \sim \sum_i x_i^{+Q} y_i^{+Q} r_i^* - \sum_i x_i^{-Q} y_i^{-Q} r_i^* \quad (2)$$

which are treated like $(\partial \alpha / \partial Q)$. From these the relative RA—AMs for the different vibrations and the depolarization factor are calculated for each vibration. This procedure which makes use of the analogy with respect to dimensions and values of molecular volumes and polarizabilities, has already been described¹⁴. It was shown, however, that by using the same 'atomic radius' for the same kind of atoms the influence on the AM is much larger for the atoms which have a larger distance from the centre of gravity. To compensate for this effect, the 'atomic radius' is divided by the square of the Euclidian distance of the atom from the centre of gravity to give a relative atomic radius of the atom i , r_i^* (equation 3)

$$r_i^* = \frac{r_i^0}{x_i^2 + y_i^2 + z_i^2} \quad (3)$$

The parameters used for the calculation of the activity measure, namely the charges and the radii of the atoms, determine the relative AMs of the vibrations. It is recommended to take as charges those which are calculated by quantum mechanical methods. If these are not known, the relative electronegativities of the atoms can be used. For the Raman activity measure the 'atomic radii' are needed. They can be the van der Waals radii but also the cube roots of the atomic polarizabilities seem to be useful.

The symmetry of the vibrations is shown by the nonzero components of the IR- and RA—AMs. Therefore, it is not necessary to define symmetry coordinates. However, in order to reproduce precisely the predictions of the

selection rules the Cartesian coordinates must be determined precisely and all steps of the program package from LIM to CAR should be calculated with 'double precision' (on IBM 3081 D). ACT also calculated sign and magnitude of the IR—CD and the Raman CID activity measure (IR—CD—AM, RA—CID—AM) for chiral molecules^{14,18}.

The APL program calculates, with the frequencies and the AMs as input, AM-spectra and AM-difference spectra. The program was developed by H. Henning, Essen and calculates, with a given halfwidth, Lorentz-profiles for each vibration. A standard output is a collection of the IR—AM-spectrum and two Raman-AM-spectra, for polarization perpendicular and parallel to the direction of excitation. For a series of molecules the IR and Raman activity spectra can be calculated and also difference spectra, showing the change of frequencies and activities with the change of molecular parameters (bond lengths, angles, force constants). Such spectra are intended to help interpret the difference spectra usually derived by the FTIR instruments or the Raman difference spectra as described by Laane and Kiefer¹⁹.

Finally VPL, a program developed by R. Schneider²⁰ draws using CAL-COMP routines the molecules in perspective and the eigenvectors as arrows.

All six programs are organized to cooperate with minimal manual input. For easy control of the correctness of the input, the CDX program prints the internal coordinates and the Z-Matrix with the definition of the force constants and VPL draws the molecules in perspective for the control of the Cartesian coordinates. The present package treats molecules with 60 atoms. It is written in FORTRAN 77 and contains about 6000 statements³⁰. The CPU time for the whole package is of the order of 100 seconds (on IBM 3081 D). A package for minicomputers is being prepared.

For the calculation of a series of spectra with changing structural parameters only the significant structural data in the input of LIM and/or the force constant values as input of CAR have to be modified.

SPSIM can be applied to many structural problems in organic chemistry. Some brief examples will now be considered. Details of definition of internal coordinates, force constants and their values are not given since they are standard for all kinds of normal coordinate calculations¹⁰.

3. EXAMPLES OF THE APPLICATION OF SPSIM

(a) *trans-Stilbene*

A force field for *trans-stilbene* was set up by accepting Cyvin's force field for aromatic rings and by the introduction of further force constants for the ethylenic part from papers of Califano³ and Ansmann²¹. Figure 3 shows the definition and Table I the values of the force constants, which are somewhat adjusted to approximate the vibrational frequencies of the deuterium-substituted stilbenes of point group C_{2h} as published by Schrader and Meier²², and Meić²³. Only one interaction force constant is introduced; the torsion/torsion interaction already defined by Cyvin. As typical results Figure 4 shows for *stilbene* the C=C-stretching vibration and the in-phase-out-of-plane C—H-deformation at the aromatic rings. The observed frequencies are 1641 and 523 cm^{-1} ²² and the values calculated 1638 and 532 cm^{-1} . Figure 4a and b show, in addition to the forms of vibrations, the elements of the Jacobi

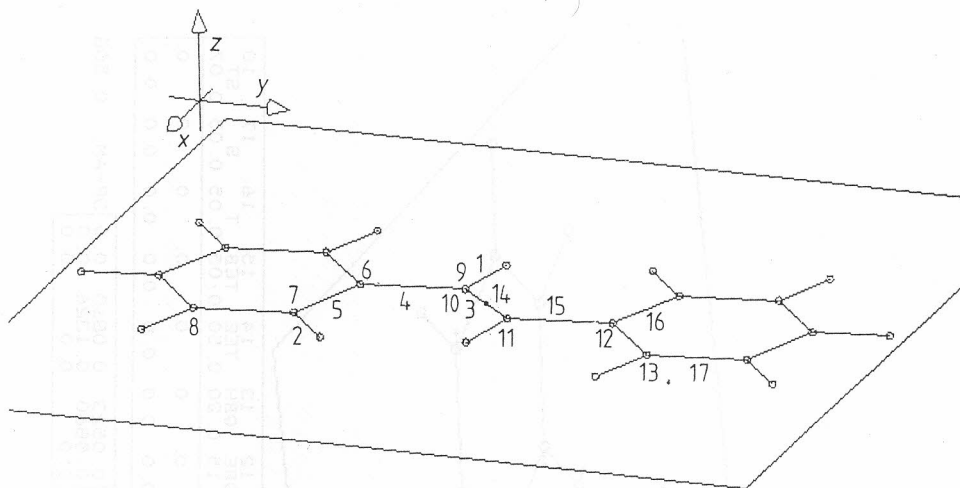


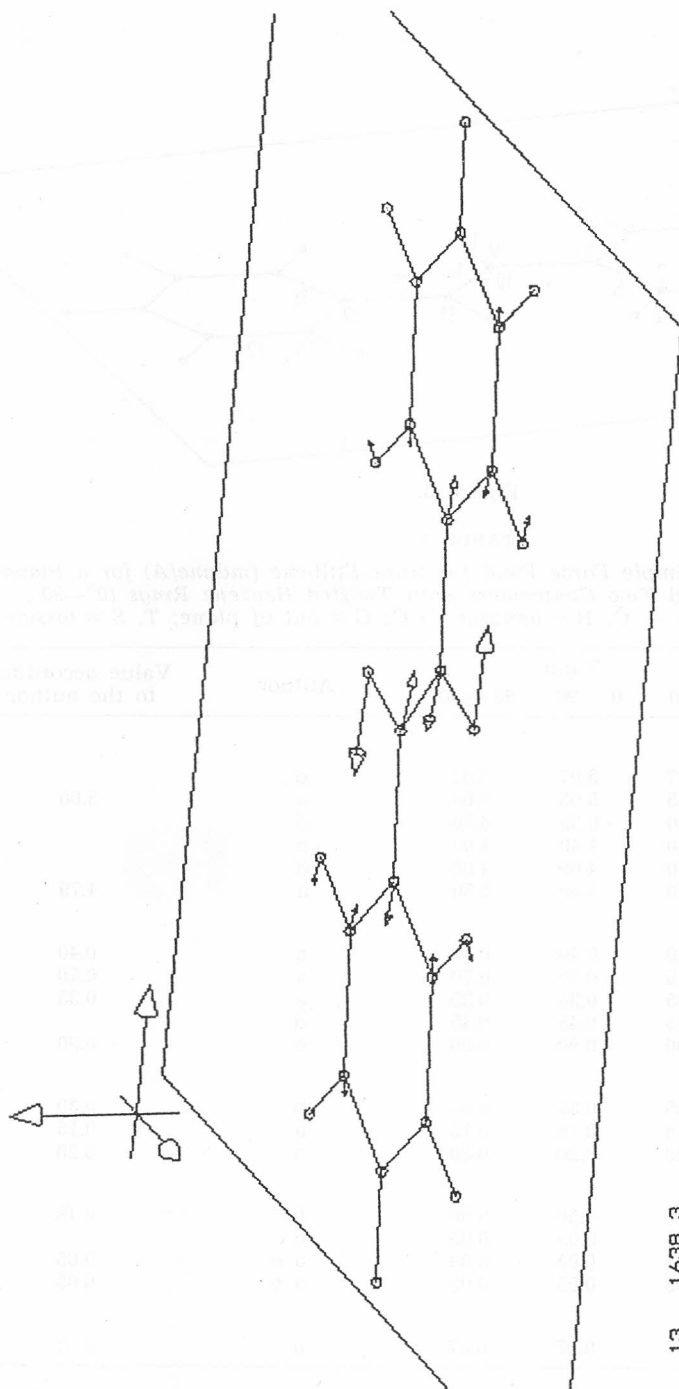
Figure 3.

TABLE I

Force Constants of a Simple Force Field for *trans*-Stilbene (mdyne/Å) for a Planar Molecule ($0^\circ-0^\circ$) and Two Conformers with Twisted Benzene Rings ($0^\circ-90^\circ$, $90^\circ-90^\circ$); E = ethylene — C; B = benzene — C; G = out of plane; T, S = torsion

No.	Name	Value			Author	Value according to the author
		$0^\circ-0^\circ$	$0^\circ-90^\circ$	$90^\circ-90^\circ$		
Stretching						
1	E—H	5.07	5.07	5.07	d	
2	B—H	5.05	5.05	5.05	a	5.00
3	C=C	5.90	6.30	6.70	d	
4	E—B	4.40	4.40	4.00	d	
	E'—B'	4.40	4.00	4.00	d	
5	B—B	5.50	5.50	5.50	a	4.79
In-plane bending						
6	EBB	0.40	0.40	0.40	a	0.40
7	BBB	0.70	0.70	0.70	a	0.70
8	BBH	0.35	0.35	0.35	a	0.35
9	BEH	0.45	0.45	0.45	d	
10	BEE	0.90	0.90	0.90	c	0.90
Out-of-plane bending						
11	GEH	0.35	0.35	0.35	b	0.30
12	GBE	0.15	0.15	0.15	a	0.15
13	GBH	0.20	0.20	0.20	a	0.20
Torsion						
14	TEE	0.50	0.50	0.50	b	0.48
15	TEB	0.05	0.05	0.05	d	
16	T	0.05	0.05	0.05	a e	0.05
17	S	0.05	0.05	0.05	a e	0.05
Interaction						
18	ST	0.07	0.07	0.07	a	0.07

^a Cyvin¹²; ^b Ansmann²¹; ^c Califano³; ^d this paper, ^e the torsion coordinates are of the 'boat type', defined by 4 atoms¹².



13 1638.3

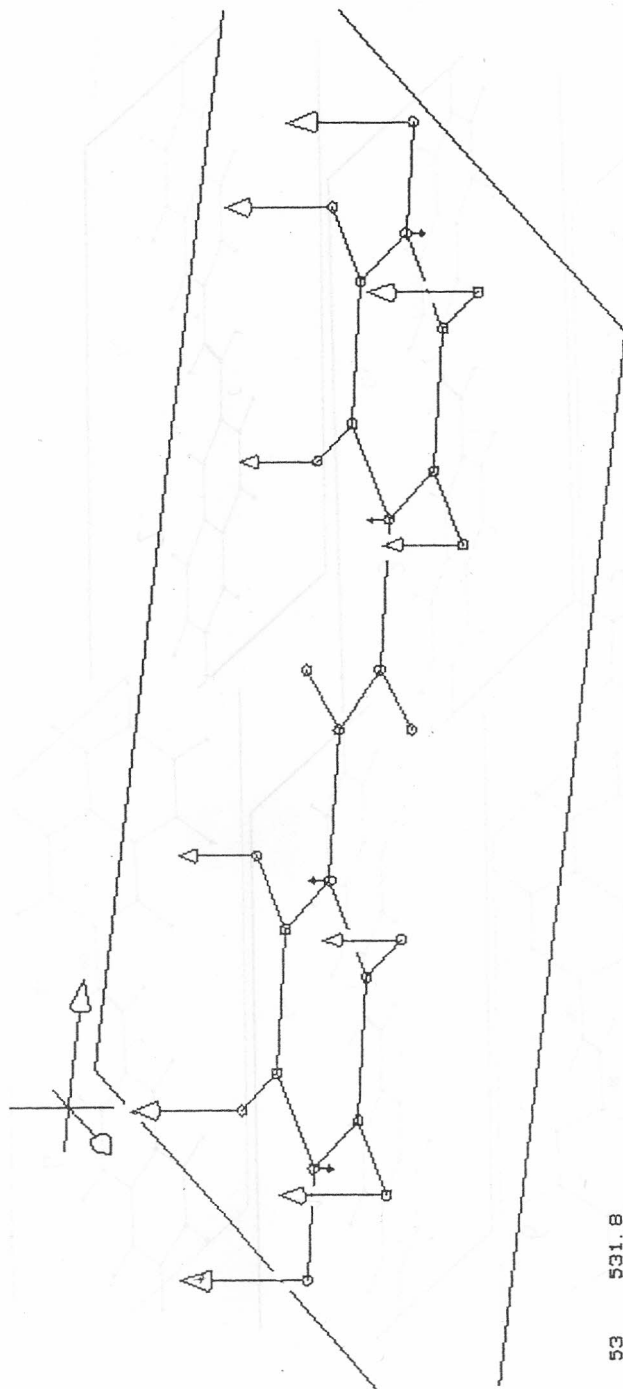
FORCE CONST	1 E-H	2 B-H	3 C=C	4 E-B	5 B-B	6 EBB	7 BBB	8 BBH	9 BEH	10 BEE	11 GEH	12 GBE	13 GBH	14 TEE	15 TEB	16 T	17 S	18 ST
	5.07	5.03	5.90	4.40	5.50	0.40	0.70	0.35	0.45	0.90	0.35	0.15	0.20	0.50	0.05	0.05	0.05	0.07
JACOBI	0.	0.	37.	49.	28.	44.	13.	90.	378.	1.	0.	0.	0.	0.	0.	0.	0.	0.
PED	0.0	0.0	26.6	26.3	19.0	2.2	1.1	3.9	20.8	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

IR-AM:	0.0	IR-AM-VECT.:	0.0
			0.0
			0.0

RA-AM:	1654.1	RA-AM-TENS.:	0.0523
			0.0860
			0.0

DP-AM:	0.508
	0.0
	0.0

Figure 4a.



53 531.8

FORCE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
CONST	E-H	B-H	C=C	E-B	B-B	EBB	BBB	BBH	BEH	BEE	GBH	GBE	GBH	TEE	TEB	T	S	ST
	5.07	5.05	4.40	5.90	4.40	0.70	0.35	0.45	0.90	0.35	0.15	0.20	0.50	0.05	0.05	0.05	0.07	
JACOBI	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.	6.	44.1136.	4.	0.	56.	936.	-312.	
PED	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	2.5	85.4	0.8	0.0	1.1	17.6	-8.2

IR-AM: 14301.9 IR-AM-VECT.:

0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0
0.0268	0.0	0.0	0.0

 RA-AM: 0.0 RA-AM-TENS.:

0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0

 DP-AM: 0.0

Figure 4b.

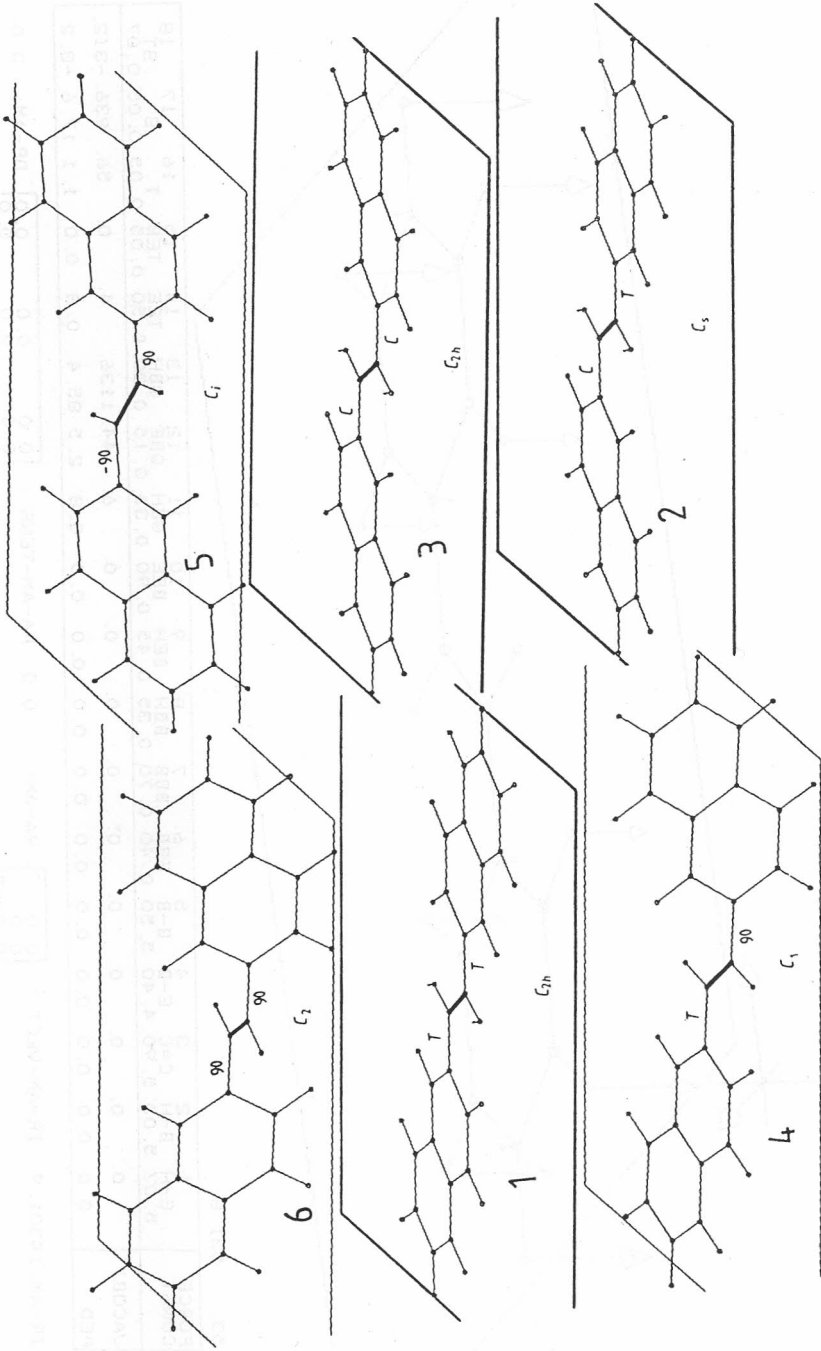


Figure 5.

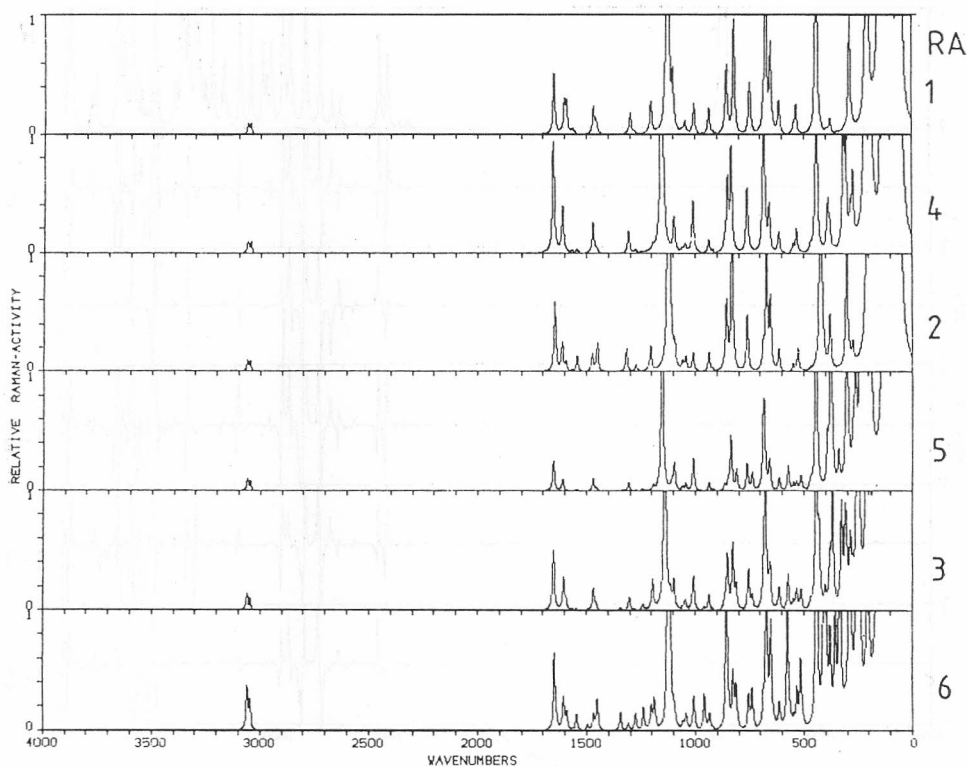


Figure 6.

matrix and the potential energy distribution (PED) together with the IR and Raman AM and its components.

(b) Conformers of Dinaphthylene

SPSIM was then applied to the dinaphthylene conformers, shown in Figure 5. The force field suitable for stilbene was transferred without change. As an example in this paper only the Raman activity spectra of all compounds and the IR activity spectrum of the *s-trans-trans*-compound and the differences of this spectrum minus spectra of the other conformers are shown in Figures 6 and 7.

The application to the problem of rotational isomers of this molecule as suggested by its fluorescence spectra²⁴ will be reported in a forthcoming publication.

(c) Conformers of Peptides

The construction of bio-mimetic molecules, synthetic molecules with properties similar to bio-molecules has to take into account the dependence of the conformation on the environment. Therefore X-ray structure determinations will not usually reveal the structures in media of different polarity.

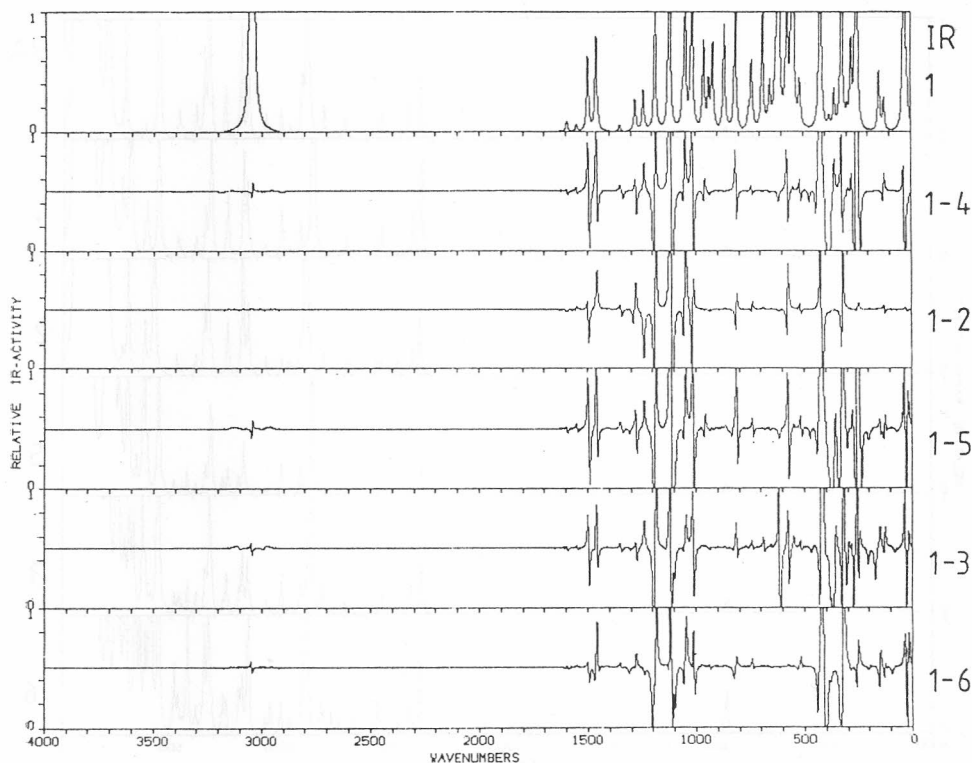


Figure 7.

Calculations of the molecular energy by molecular mechanics give information on the relative energy of conformers^{26,27}. Nevertheless, these calculations usually do not consider polar properties of solvents, either. Vibrational spectroscopy may give information about the structure of conformers. However, this information is coded by band frequencies, intensities and their changes with a change of the environment. In order to deal with such problem, we calculated the infrared frequencies and AMs of seven conformers of an ionophor, a mesitylene, substituted with 3 dipeptide chains (Figure 8).

We used the set of 72 force constants of a simplified general valence force field of polymeric amino acids, published by Krimm²⁸ together with the force constants for the benzene ring, given by Cyvin¹². The influence of C=O...H—N hydrogen bonds were taken into account by the typical dependence of their force constants on the bonds length, as described, for instance by Novak²⁹. The question was: Which of the 7 conformer structures defined by a minimum in the energy hypersurface represents the molecule in a non-polar medium? The significant parts of the IR spectrum of the sample in CCl₄ is reproduced as insert in Figure 9, which shows the simulated IR—AM-spectra of the 7 conformers of the lowest energy with their energy given by numbers in the figure. As a result there is a large probability that the conformer with the second-lowest energy is that which is represented by the

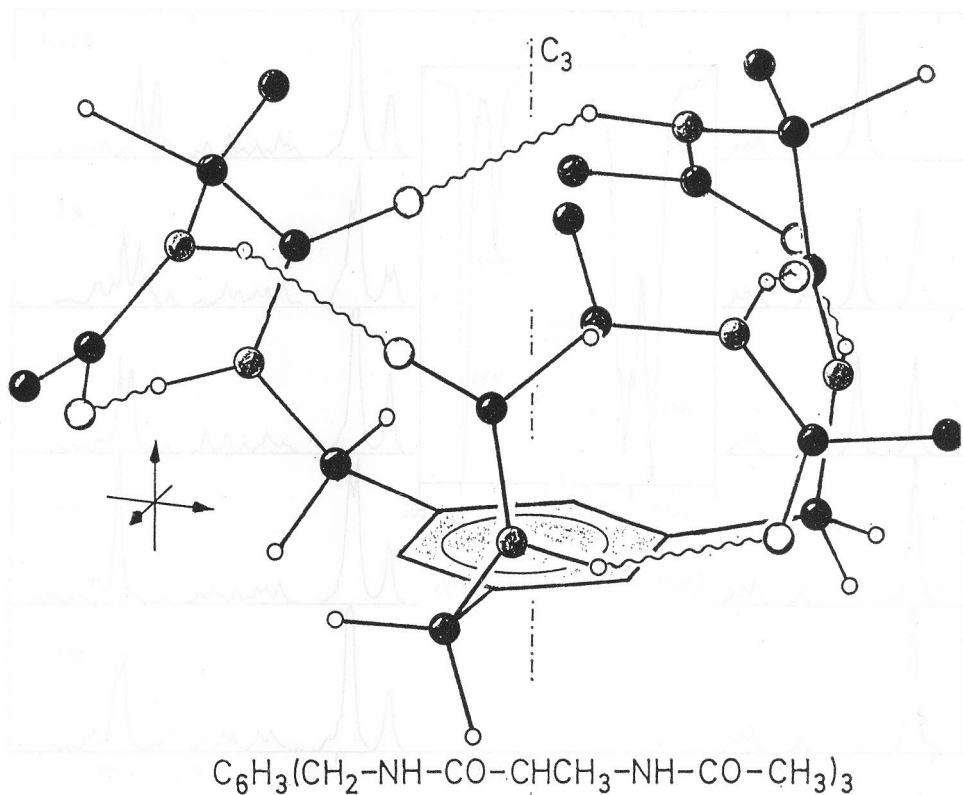


Figure 8.

infrared spectrum. A detailed account of this procedure will be given elsewhere.

4. CONCLUSION

The intention of this work is to supply the organic chemist using vibrational spectroscopy with a tool which is comparable to the Hückel method for quantum-chemical calculations. It is intended to reveal the change in frequencies and intensities which occur when structural parameters are changing. The basic approach is quite crude — simplified force fields and activity measures — but at the expense of a longer CPU time more interaction force constants may be included and for small molecules SPSIM can be combined with a modified CNDO or MNDO or even *ab initio* procedure which calculates approximate IR and Raman intensities⁷.

Acknowledgement. — The author wishes to thank Prof. Fischer, Rehovot, Israel, for the invitation to work at the Weizmann Institute, Prof. Fischer and A. Shanzer, Rehovot, for providing interesting problems and for many discussions, C. Felder for supplying the Cartesian coordinates, his present and former co-workers who developed some of the programs (D. Bougeard, M. Spiekermann, H. Henning, R. Schneider and P. Fischer), Ruth Eisenberg and Hans Jarosch from the Computer Center of the Weizmann Institute for valuable help, Derek Long, Bradford, GB, for advice

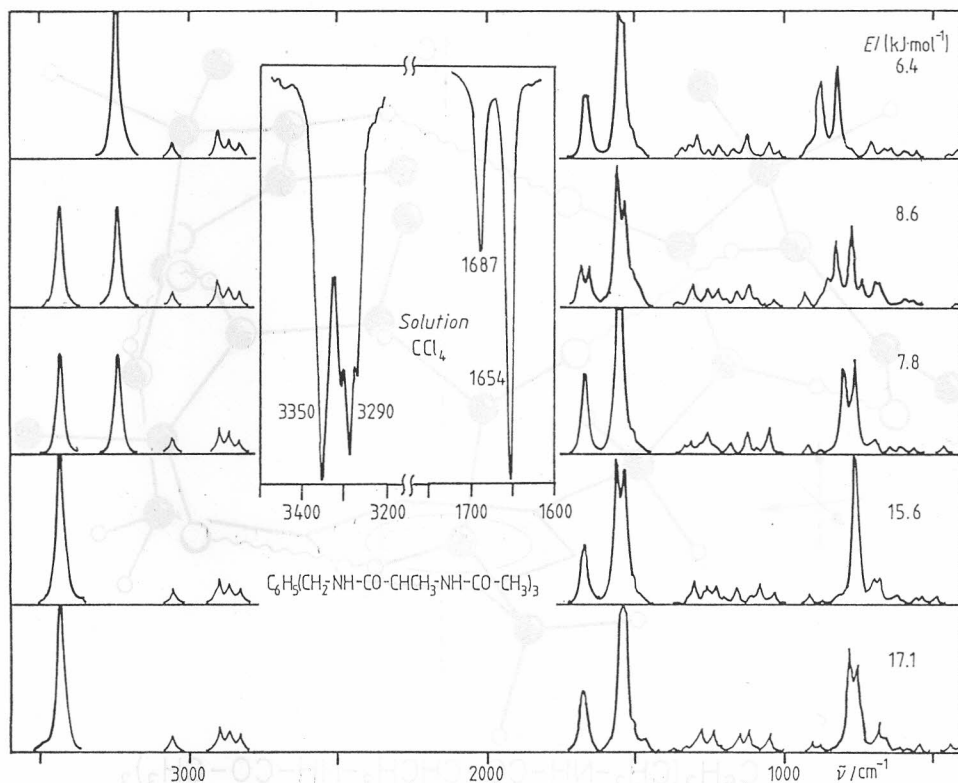


Figure 9.

concerning the manuscript, the Minerva foundation for a scholarship, and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for considerable financial help.

REFERENCES

1. R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta* **19** (1963) 85, 117; **21** (1965) 169.
2. D. C. McKean, J. L. Duncan, and L. Batt, *Spectrochim. Acta* **29A** (1973) 1037.
3. S. Califano, *Pure Appl. Chem.* **18** (1969) 353.
4. T. Shimanouchi, *Vibrational Spectroscopy and its Chemical Applications*, Collection of the Scientific Papers of Takehiko Shimanouchi, The University of Tokyo, 1977.
5. M. Gussoni, chapter 5 in (13): *Infrared Intensities by Parametric Methods, A Guided Tour*; chapter 11 in reference 13: *Raman Intensities by Parametric Methods, A Guided Tour*.
6. L. A. Gribov, *Intensity Theory for Infrared Spectra of Polyatomic Molecules*, Consultants Bureau, New York 1964.
7. M. Spiekermann, D. Bougeard, H.-J. Oelichmann, and B. Schrader, *Theor. Chim. Acta* **54** (1980) 301; P. Fischer, *Berechnung der Intensitäten von Schwingungsspektren mit einem erweiterten MNDO-Verfahren*, Diplomarbeit, Essen 1985.
8. B. Schrader and A. Ansmann, *Angew. Chemie* **87** (1975) 345; *Int. Ed.* **14** (1975) 346.

9. H.-J. Oelichmann, D. Bougeard, and B. Schrader, *Angew. Chemie* **94** (1982) 648; *Int. Ed.* **21** (1982) 639; *Angew. Chemie Suppl.* **8** (1982) 1404.
10. S. Califano, *Vibrational States*, John Wiley & Sons, London 1976.
11. P. 249 in reference 10
12. S. J. Cyvin, *J. Mol. Struct.* **79** (1982) 423.
13. W. B. Person and G. Zerbi (Eds.), *Vibrational Intensities in Infrared and Raman Spectroscopy*, Elsevier, Amsterdam 1982.
14. B. Schrader, M. Spiekermann, L. Hecht, und D. Bougeard, *J. Mol. Struct.* **113** (1984) 49.
15. T. Shimanouchi, *Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules*, The University of Tokyo, 1968.
16. J. Brandmüller and H. Moser, *Einführung in die Ramanspektroskopie*, Steinkopff, Darmstadt 1962.
17. E. B. Wilson Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra*, McGraw-Hill, New York 1955.
18. L. Hecht and B. Schrader, in preparation.
19. J. Laane and W. Kiefer, *Appl. Spectrosc.* **35** (1981) 428.
20. R. Schneider, *Messung und Berechnung der Infrarot- und Raman-aktiven Molekül- und Gitterschwingungen des kristallinen Melamins*, Dissertation, Dortmund 1974.
21. A. Ansmann, *Schwingungsspektroskopische Untersuchung der Konformation monocyclischer und offenkettiger konjugierter Diene*, Dissertation, Dortmund 1974.
22. B. Schrader and W. Meier, *Raman/IR-Atlas of Organic Compounds*, **2**. Vols., Verlag Chemie, Weinheim 1974—1976.
23. Z. Meić and G. Güsten, *Spectrochim. Acta* **34A** (1978) 101.
24. E. Fischer, *J. Mol. Struct.* **84** (1982) 219.
25. P. Fischer, A. Grunenberg, D. Bougeard, B. Schrader, *J. Mol. Struct.* **146** (1986) 51.
26. S. Lifson, C. E. Felder, A. Shanzer, and J. Libman, *Biomimetic macrocyclic molecules: An interactive theoretical experimental approach in: Progress in Macrocyclic Chemistry*, Vol. 3, Wiley-Interscience, in press.
27. A. T. Hagler, E. Huler, and S. Lifson, *J. Amer. Chem. Soc.* **96** (1974) 5319.
28. S. Krimm, *Biopolymers* **22** (1983) 217; A. M. Dwivedi and S. Krimm, *Macromolecules* **15** (1982) 177 and 186; *Biopolymers* **23** (1984) 923; *J. Phys. Chem.* **88** (1984) 620.
29. A. Novak, *Structure and Bonding* **18** (1974) 203.
30. P. Fischer, D. Bougeard, M. Spiekermann, L. Hecht, R. Schneider, H. Henning, and B. Schrader, in preparation.

SAŽETAK

Spregnuti proračuni vibracijskih frekvencija i intenziteta. X. Proračun frekvencija i infracrvenih i Ramanovih intenziteta za velike molekule

Bernhard Schrader

Paket programa SPSIM može pomoći organskim kemičarima da bi bolje iskoristili informacije o strukturi velikih molekula skrivena u vibracijskim spektrima. Program je napisan na jeziku FORTRAN 77. SPSIM ne može točno reproducirati eksperimentalne spektre, nego je prije oruđe koje otkriva promjene u spektrima kada se mijenjaju topologije, geometrija ili raspored veza u molekuli. Osim frekvencija SPSIM računa za svaku vibraciju mjeru aktivnosti (AM) svake komponente vektora dipolnog momenta i tenzora polarizabilnosti, relativne AM-vrijednosti vrpce u infracrvenom i Ramanovu spektru, kao i depolarizacijske faktore temeljene na AM. Vrijednosti AM su nula za zabranjene vibracije, a kada su velike, dotični zapaženi intenziteti obično nisu mali. Proračun AM-vrijednosti čak i za velike molekule zahtijeva tek nekoliko sekundi CPU-vremena. Primjeri rezultata navedeni su za stilben, rotacijske izomere dinaftiletilena i konformacijske izomere fleksibilnih peptida.