

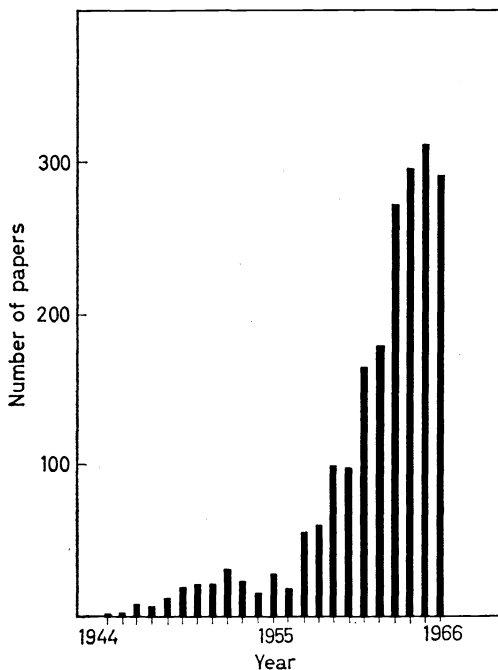
# FORCE FIELD OF LARGE MOLECULES

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Lecturing on a boring subject like force constant calculations is undoubtedly one of the quickest ways of putting even the most resistant audience asleep, since the only thing one can do is to present a series of slides filled with calculations which are usually interesting only for the person who has performed the calculations and for the very few others who are by chance involved in the same problem. In my case, the situation is made worse by the fact that this lecture is slightly out of date—roughly three or four years. At that time, in fact, force constant calculations were still a field for specialists and words such as G matrix or Jacobian still had the power to fascinate people. The ‘consumers society’ has rapidly destroyed the magic power of these words. Today almost all laboratories have their own computer programmes at their disposal, usually a copy of the original one by Schachtschneider and Snyder, and even our old ‘Bible’, the book by Wilson, Decius and Cross, can be found in any supermarket.

The result of this situation is shown in *Figure 1* where the number of



*Figure 1*

papers dealing with force constant calculations published each year, in the last twenty years, is shown in graphic form.

In such circumstances it would be pointless to outline the details of the mathematical treatment of molecular vibrations and so I shall assume that everybody here is acquainted with the mathematical machinery. Rather, I want to discuss those problems which have already been settled in the last few years and those which are still open to future developments, using a few selected examples from our laboratory. Before entering the subject, I wish however to make a small comment on the impact of force-constant calculations in massive quantity on the mental attitude of molecular spectroscopists. It is my opinion that this influence has been positive. Concepts which were commonly used a few years ago are today almost completely abandoned. For instance the description of vibrational modes in terms of group vibrations, stretching, bending, rocking and so on, is more and more often replaced by the description in terms of potential-energy distribution. Tentative vibrational assignments, so common before, are replaced by *a priori* prediction of the spectra, through transfer or force field, which even if not free from danger, are certainly more reliable by several orders of magnitude.

Let us now start with a look at the technical developments which, in the last few years, have made possible the extension of force-constant calculations to large molecular systems.

- (a) the development of iterative methods for the automatic refinement of force constants,
- (b) the understanding of redundancies,
- (c) the development of overlay techniques for the refinement of a force field common to several related molecules.

All these features are included in the basic form of several computer programmes and currently used for actual calculations. It is therefore unnecessary to discuss them in detail, even if some aspects are still unsatisfactory and further work is needed. Convergence of the refinement, unicity of the solution and errors in the force constants are in fact technical questions which still deserve attention. In this respect I wish to call your attention to the fact that recently some attempts have been made to find a direct solution of the secular equation, by-passing the iterative method<sup>1</sup>. All these methods however, either explicitly or implicitly, introduce severe constraints on the force field so that, for the moment, they cannot be considered as a substitute for the iterative refinement.

However, an interesting technical development has been presented at this meeting by Doctor Zerbi concerning the automatic generation in a computer of the  $U$  matrix for the construction of symmetry coordinates. Since the  $U$  matrix for a large molecule is a major part of the input data this procedure will certainly speed up the process and reduce the possibility of errors. Now, in order to discuss the basic problems related to the force fields of large molecular systems, let me specify what I mean by 'large molecule'. It seems obvious that, as far as the size is concerned, it is difficult to draw a sharp dividing line between small and large molecules. I shall instead use an operative definition which is concerned essentially with the kind of problems one has to face.

**SMALL MOLECULES**

For small molecules the vibrational assignment is well established, often for several isotopic species. In addition, the molecular geometry is well known and many additional data, such as Coriolis coupling and centrifugal distortion constants are available or are, in principle, experimentally accessible. Finally, the dimension of the secular equation is small and therefore does not constitute a problem by itself. The consequence of this situation, i.e. number of data at disposal plus limited dimension of the problem, is that the most general harmonic field for these molecules involves a number of force constants normally lower or at least equivalent to the number of experimental data available. Research in this case is essentially oriented towards the determination of a complete potential function and the emphasis is on the unicity of the solution, on the nature of the force field and on the validity of the harmonic approximation. Non-harmonic force fields, including cubic and quartic terms have been derived in a number of cases and it looks as if a great deal of attention will be devoted to this aspect in the near future.

**LARGE MOLECULES**

For large molecules the vibrational assignment is normally not completely established and the molecular geometry is often known only approximately. Only in a few cases are the frequencies of a deuterated species available, whereas Coriolis and distortion constants are not experimentally accessible. The secular equation includes symmetry blocks of noticeable dimensions, the solution and building up of which requires a great deal of computer time.

As a consequence the most general harmonic field for these systems includes a number of force constants which largely exceeds the number of experimental data and is in any case impractical. The essential aspect of this kind of work is therefore the search for approximate potential functions including a practical number of terms, the emphasis being on the heuristic power of such potential function in establishing vibrational assignments and in predicting spectra of more complex molecules of the same class.

If one analyses the work done in the last few years in the area of large molecules, one realizes that three main problems did actually emerge which have already been partially solved and which partially underline the future developments. These problems can be summarized as follows:

- (i) type of force field
- (ii) validity of approximate fields
- (iii) transfer of force constants.

Let us discuss the first problem, namely, which is the best force field for a large molecule. Unfortunately when one tries to discuss this point, one automatically gets involved in an argument between supporters of the two most-used force fields, the UB and the GV force fields. For small molecules other force fields such as the orbital following<sup>2</sup> or Mills' field<sup>3</sup> have been proposed, but their use has not been extended to large molecules.

As far as the UBFF and the GVFF are concerned, both are legitimate fields and in fact both have been successfully used in the prediction of spectra of

large molecules. Some people have questioned the introduction of the linear terms in the UB force fields. Others have pointed out that it is bound to an unrealistic molecular model. None of these criticisms is however sufficient to balance the fact that in practice the UBFF works. The really important point is that the UBFF is by definition an approximate field, with given characteristics and limitations, whereas the GVFF, at least in principle, is of a general nature.

The UBFF can in fact be considered mathematically as a particular kind of the GVFF in which a set of constraints exists between the off-diagonal terms, some constants being automatically set equal to zero and others related by linear equations. Since the UBFF is a specific case of the GVFF, one should have no doubts in deciding which one is better. Unfortunately a real GVFF is, for a large molecule, only an abstraction, since all the available ones are largely approximate. One must therefore compare the UBFF with approximate VFF and in this sense it is easily understood why the UBFF has achieved popularity:

(a) The consistent method by which the constraints are introduced in the  $F$  matrix, on the basis of the non-bonded atom-atom repulsion.

(b) The difficulty of assigning a quantitative physical meaning to several off-diagonal VFF constants, in terms of molecular structure.

(c) The impossibility of using the GVFF in its general form, a fact which makes all VFF of practical use comparable, in number of force constants, to the corresponding UB force field.

When the non-bonded atom-atom repulsions are expressed in terms of internal coordinates, all the VFF interactions between adjacent coordinates of the type



are originated. These interactions are generally those which, after the diagonal terms, play the most important role in the  $F$  matrix and this explains why the UBFF works for several molecules. I believe that it can be safely stated that each time the UB force field works for a molecule, the corresponding VFF of the type described above would give similar performances. Inversely, whenever the UBFF fails to work for a molecule, one can automatically assume that other interaction constants, between non-adjacent coordinates, play an important role in the  $F$  matrix. This is actually what happens for several molecular systems for which the UBFF is unable to reproduce all the observed frequencies. A well-known example is that of ethylene. An attempt to save the UBFF was made by Shimanouchi with a rather 'ad hoc' explanation involving the concept of bond-flexibility<sup>4</sup>. Later however Overend and Scherer<sup>5</sup> did show that the introduction of a *trans* bending-bending interaction constant was sufficient to put the UBFF to work. An even better example is offered by the aromatic molecules. For all aromatic systems the basic UBFF fails to reproduce the observed

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spectrum correctly, the error being concentrated in those ring modes which correspond to the famous  $B_{2u}$  ring vibration of benzene. For this molecule Overend and Scherer<sup>6</sup> suggested some years ago an elegant way of introducing into the force field the *ortho*, *meta* and *para* stretching–stretching interactions condensed in a single term, the so-called Kekulé constant. This modified UBFF works correctly and was later extended with success to naphthalene<sup>7</sup> and anthracene<sup>8</sup>.

The Kekulé constant has however nothing to do with the UBFF, being nothing else but a specific method of introducing constraints among some VFF interactions, on the basis of qualitative resonance concepts. Apart from this, there is little doubt that, once the UBFF is correctly modified, it works well. At this point however, one of the main advantages of the UBFF, namely internal consistency, is practically lost, and it is legitimate to ask why one should use an unrealistic model, properly adjusted to fit the results. In addition, owing to its greater generality, the VFF can always be chosen to give better performance, without any significant complication. In *Table 1*, for instance, two calculations are compared of the planar vibrations of

*Table 1.* Comparison of UBFF and GVFF for the planar vibrations of naphthalene

	$\nu_{\text{obs}}$	UBFF	GVFF			$\nu_{\text{obs}}$	UBFF	GVFF		
$A_g$	3055	3077	22	3069	14	3056	3076	20	3068	12
	3025	3022	3	3014	-11	3029	3022	-7	3013	-16
	1579	1568	-11	1584	5	1509	1509	0	1527	18
	1460	1450	-10	1445	-15	1361	1372	11	1372	11
	1379	1380	1	1373	-6	1209	1186	-23	1194	-15
	1144	1172	28	1170	26	1144	1135	-9	1149	5
	1025	1004	-21	1014	-11	1008	1000	-8	1008	0
	763	784	21	771	8	618	637	19	608	12
	512	485	27	511	-1					
			$\Sigma \Delta\nu_j  = 144$		97				97	
$B_{1u}$	3065	3078	13	3067	2	3055	3076	21	3066	15
	3029	3026	-3	3017	-12	2980	3026	46	3015	35
	1595	1589	-6	1591	-4	1624	1621	-3	1612	-12
	1389	1393	4	1381	-8	1436	1455	19	1436	0
	1265	1259	-6	1266	1	1240	1246	6	1254	14
	1125	1116	-9	1126	1	1099	1116	17	1114	15
	810	793	-17	798	-12	936	935	-1	939	3
	362	380	-18	361	-1	506	480	-26	495	-11
		$\Sigma \Delta\nu_j  = 76$		41				139		105

MUBFF 16 force constants  
GVFF 23 force constants

naphthalene made using respectively a MUBF<sup>7</sup> and a VFF<sup>9</sup>, showing the better results obtained in the latter case. It is true that this comparison is not fair since the UBFF had only 16 independent terms, whereas the VFF includes 23 force constants. However as many as 8 VFF interaction terms are actually stretching–stretching interactions which are efficiently replaced by a single Kekulé constant, and therefore the comparison is significant. Anyway, we have reached a stage now in which the importance of a force field for a large molecule derives from its ability to predict spectra of complex molecular systems. To do the job with sufficient accuracy a considerable sophistication of the force field is required. This sophistication, which previously did

constitute a great limitation, is today feasible and in this respect the GVFF undoubtedly offers much better possibilities. Once we have seen the advantages, let us discuss the disadvantages of the GVFF. This leads us to the second point, namely to the practical approximations necessary to make the GVFF usable for large molecules. Several approximate VFF have been worked out in these last few years for single or for entire classes of molecules. In each case, however, a different approach to the simplification of the force field has been used with a considerable overlap of personal preferences, chemical intuition and genuine mathematical selection.

There are two main kinds of approximations which have been used until now in the process of contraction of the GVFF to an approximate VFF. The first one is that all interactions of the C-H stretching with other internal coordinates can be set equal to zero without affecting the results. This approximation is by no means justified *a priori* and in fact can create a problem for the interpretation of force constants in terms of electronic structure. Furthermore it has a different effect on the light and deuterated species, since the C-D stretching bands are much closer to the skeletal vibrations than the corresponding C-H vibrations.

The second approximation is based on the idea that the interaction between two coupled springs becomes less and less important the more the two springs are separated in the vibrating system. Although this approximation is much more realistic, it fails in cases such as benzene, for which interactions between non-adjacent coordinates are made important by the resonance structures. One can ask if it is absolutely necessary to approximate a force field with a starting hypothesis of dubious validity and if it would be safer to rely only on a mathematical method.

Happily there is a method for judging the relative importance of each interaction term, through the inspection of the elements of the Jacobian matrix  $(\partial \lambda_h / \partial F_{ji})$ . Only interaction terms for which at least one element of the relative column of the Jacobian matrix is big enough, need be considered.

A more quantitative criterion for the selection of force constants has been given by Gayles, King and Schachtschneider<sup>10</sup> and is condensed in the following equations, which need no specific discussion being well known to people working in the field.

$$\begin{aligned}
 G(F_0 + \Delta F)L &= LA \\
 F &= Z\phi & \Delta\lambda &= JZ\Delta\phi \\
 (JZ)'P\Delta\lambda &= (JZ)'P(JZ)\Delta\phi \\
 S_0^2 &= \Delta\lambda'P\Delta\lambda \\
 S^2(\lambda) &= (\Delta\lambda - JZ\Delta\phi)'P(\Delta\lambda - JZ\Delta\phi) = S_0^2 - D'C^{-1}D \\
 D &= (JZ)'P\Delta\lambda & C &= (JZ)'P(JZ)
 \end{aligned}$$

The standard deviations in the element of  $\phi$  are given by

$$\begin{aligned}
 \sigma^2(\phi_i) &= C_{ii}^{-1} \sigma^2(\lambda) \\
 \sigma^2(\lambda) &= S^2(\lambda)/(n - f)
 \end{aligned}$$

$n$  being the number of frequencies and  $f$  the number of force constants. If we change only the  $i$ th force constant, the reduction in the square error is given by

$$\Delta S_i^2 = C_{ii}^{-1} D_i^2$$

and the standard deviation in  $\varphi_i$  is given by

$$\sigma(\varphi_i) = C_{ii}^{-\frac{1}{2}} \sigma(\lambda)$$

These two last equations can be used to estimate the sensitivity of the frequencies to a given force constant. If one defines two arbitrary constants  $\epsilon_1$  and  $\epsilon_2$ ,  $\varphi_i$  needs to be included only if

$$S_0^2/(n-f) > \Delta S_i^2/(n-f+1) > \epsilon_1$$

$$\sigma(\varphi_i) - \varphi_i < \epsilon_2$$

The risk of using this method is that it neglects correlations of adjustment in the force constants, but it can be considered satisfactory for discovering which force constants determine the frequencies.

Even for moderately complicated molecules the iteration method often fails to converge, since in the relation

$$(\mathcal{J}\mathcal{Z})'P\Delta\lambda = (\mathcal{J}\mathcal{Z})'P(\mathcal{J}\mathcal{Z})\Delta\phi$$

$$D = C\Delta\phi$$

$$\Delta\phi = C^{-1}D$$

the matrix  $C$  is often singular, and therefore cannot be inverted. We have found that a faster method of refinement<sup>11</sup> which avoids these difficulties is as follows: from the equations written above, the square error before and after a cycle of refinement is given by:

$$S_0^2 = \Delta\lambda'P\Delta\lambda$$

$$S^2(\lambda) = S_0^2 - D'C^{-1}D = S_0^2 - D'\Delta\phi$$

therefore

$$\Delta S^2 = S^2(\lambda) - S_0^2 = -D'\Delta\phi = -\Delta\lambda'P(\mathcal{J}\mathcal{Z})\Delta\phi$$

In order to achieve a convergence we want  $\Delta S^2$  to be big and negative and therefore it is necessary that

$$\Delta\phi = N(\mathcal{J}\mathcal{Z})'P\Delta\lambda$$

where  $N$  is a constant properly chosen.

If we adjust only one constant  $\varphi_i$ , the reduction in the error is given by:

$$\Delta S_i^2 = -(\Delta\lambda'P\mathcal{J}\mathcal{Z})_i\Delta\varphi_i = -(\Delta\lambda'P\mathcal{J}\mathcal{Z})_i^2N$$

and therefore the elements of

$$(\Delta\lambda'P\mathcal{J}\mathcal{Z})^2$$

give a direct indication of the importance of the elements of  $\phi$  in adjusting the frequencies.

In principle, one could apply this method from the beginning since it can easily be adapted as a sub-routine in an electronic computer. An example is the multiple regression sub-routine used by Schachtschneider and Snyder<sup>12</sup> for the refinement of the force field of aliphatic hydrocarbons. There are however two severe limitations to the generalisation of this procedure. The first is that it is almost impossible to analyse, one by one, the several hundreds of interaction terms which occur in the  $F$  matrix of a large molecule. The second is that the number of interaction terms which would pass the test is still much bigger than the number of experimental data available. It is therefore essential first to speed up the search for the important terms and, second, to compress groups of them into single terms. A systematic way of doing this is as follows: first, all interaction terms are divided into groups, according to the type of coordinates which interact, and a single force constant is assigned to each group. Even for large molecules this amounts to a limited number of terms. For instance the 327 terms of the planar  $F$  matrix of a molecule like naphthalene can be classified as shown in *Table 2*.

*Table 2.* Classification of the interaction force constants of naphthalene

	<i>I coord.</i>	<i>II coord.</i>	<i>No.</i>		<i>I coord.</i>	<i>II coord.</i>	<i>No.</i>	
	CC	CH	4	2				
	CC	CC	4					
	CH	CCH	4	3				
	CC	CCH	4					
	CC	CCC	7					
	CCH	CCH	2	3				
	CCC	CCH	4					
	CCC	CCC	2					
	CH	CCC	2	3				
	CC	CCH	4					
	CC	CCC	2					
	CH	CH	2	3				
	CH	CC	5					
	CC	CC	6					
	CH	CCH	3	4				
	CH	CCC	5					
	CC	CCH	5					
	CC	CCC	9					
	CCH	CCH	2	3				
	CCH	CCC	5					
	CCC	CCC	6					
	CH	CH	2	3				
	CH	CC	7					
	CC	CC	5					
							168	38
					6 atoms		77	20
					7 atoms		44	17
					8 atoms		22	10
					9 atoms		2	2
							145	49
							313	87

Only the first 168 terms are shown in detail and it is seen from the table that they can be grouped into 38 groups. With this initial set a first Jacobian is constructed and searched for unimportant terms. In this way entire groups of force constants can be eliminated at once, thus reducing considerably the time and computer space required for the complete search. As a second step each of the retained groups of force constants is split into its components which are analysed with a new Jacobian. Again at this stage a cut-off of unimportant terms, which were masked in the first step, is achieved. As a final step, all terms which give similar contributions to the Jacobian matrix are collected together. This systematic process of compression has never been used in full until now, although in many cases it has been used on force fields already approximated from the beginning. Despite the appeal of simplified models, justifiable only *a posteriori*, I believe that for the future we need to reduce to a minimum the impact of personal preferences on the form of force fields and therefore, unless new solutions of a completely different nature are found, we should rely only on the Jacobian matrix for the elimination of force constants.

The third problem we have to discuss is the possibility of transfer of force constants from one molecule to another. I believe that the work accumulated in the last few years has given a definite answer to this question. Force fields are transferable and can be used to predict spectra of complex molecules and to study the conformational structure of molecules. This last point is of very great importance and I believe that it alone could justify the use of approximate force fields. It is in fact the only efficient method for the study of conformational structure in the liquid state and I have few doubts that the future will witness a great development of such researches. Before presenting some data to justify this point I wish to clarify the meaning of the word 'transferable'. Let us assume that we have at our disposal a good force field for a molecule *A* and that we wish to predict with this field the spectrum of molecule *B* closely related to *A*.

The following limiting possibilities can occur:

- (a) There is no variation of bond lengths and angles in going from *A* to *B*. An example is offered by the series of aliphatic hydrocarbons and by the transfer of their force constants to linear polymers.
- (b) There is no variation of bond lengths but there is a change of conformation. In this case there are some interaction terms which are conformation dependent and therefore either this must be taken care of, or any conclusion, drawn from the transfer, must take into account some deviations for those frequencies which are more sensitive to these interactions. An example would be the transfer of force constants from the aliphatic hydrocarbons to *cyclopentane* in which four  $\text{CH}_2$  groups are in a *cis* instead of *trans* position.
- (c) Both bond lengths and angles change. In this case the transfer is less accurate and the prediction of the spectrum needs to be judged with more criticism. An example would be the transfer of the force field of benzene to naphthalene or anthracene.

Let me now give a few examples of transferability taken from the work done in our laboratory. For the sake of brevity I shall confine myself to the transferability of the valence force field.

It is, however, necessary to make clear that the same is true for the UBFF and that many examples of transferability have been collected by Dr. Shimanouchi and his group<sup>13</sup>.

The first field to meet all the requirements for complete transferability was proposed by Schachtschneider and Snyder<sup>12</sup> for aliphatic hydrocarbons. The excellent performance of this force field is so well known that it is unnecessary to comment on it further.

In our laboratory, starting with this aliphatic field, we have worked out another force field of general use for the *cycloolefins* with isolated *cis* or *trans* double bonds.

Table 3. Comparison between the observed and the zero-order calculated spectrum of *cyclohexene-d<sub>0</sub>*

<i>I.R.</i> (gas)	<i>I.R.</i> (liq.)	<i>Raman</i> (liq.)	<i>Calc.</i>	<i>N</i>
	175 vs	175 (1.5) dp	186 <i>B</i>	42
	280 w	281 (4.5) dp	285 <i>A</i>	22
	393 vw	394 (10) p	399 <i>A</i>	21
450 m	452 s	455 (2.5) dp	474 <i>B</i>	41
		495 (3) dp	521 <i>A</i>	20
636 vs	640 vs	643 (2) dp	634 <i>B</i>	40
660 s	670 m		<i>B</i>	42 +
718 vs	720 vs	721 (1.5) dp	706 <i>B</i>	39
		789 (2) p	779 <i>A</i>	19
810 w	810 w		<i>A</i>	40 + 42
		822 (40) p	811 <i>A</i>	18
877 s	878 m	878 (3) dp	869 <i>B</i>	38
	905 w	905 (9) p	902 <i>A</i>	17
919 s	917 m		907 <i>B</i>	37
		966 (4.5) dp	973 <i>A</i>	16
	998 vw		<i>B</i>	42 + 18
1009 w	1009 w		967 <i>B</i>	36
1039 s	1038 m	1040 (8) dp	1043 <i>B</i>	35
	1068 vw	1068 (12) dp	1054 <i>A</i>	15
			1084 <i>A</i>	14
	1112 vw		<i>B</i>	21 + 39
1140 vs	1138 s	1139 (3.5) dp	1131 <i>B</i>	34
	1222 vw	1222 (40) p	1233 <i>A</i>	12
1240 m	1241 w	1241 (11) p	1250 <i>A</i>	11
			1227 <i>B</i>	33
1269 m	1264 m	1265 (15) dp	1278 <i>B</i>	32
	1310 w		<i>B</i>	39 + 20
1325 m	1321 m		1357 <i>B</i>	31
1343 m	1338 w		1425 <i>B</i>	30
		1343 (5) p	1369 <i>A</i>	10
	1350 w	1353 (5) p	1403 <i>A</i>	9
	1392 m		<i>B</i>	42 + 12
			1435 <i>A</i>	8
1445 vs (sh)	1438 vs	1436 (40) p	1454 <i>A</i>	7
1450 s	1447 s		1446 <i>B</i>	29
1455 vs	1456 s	1455 (20) dp	1467 <i>B</i>	28
	1530 vw		<i>B</i>	21 + 34
1660 m	1653 s	1656 (40) p	1687 <i>A</i>	6
	2840 vs	2839 (30) p	2854 <i>A</i>	5
2858 vs	2860 vs		2853 <i>B</i>	27
		2865 (21) p	2855 <i>A</i>	4
2878 vs	2882 vs	2886 (19) dp?	2854 <i>B</i>	26
	2929 vs	2916 (40) p	2925 <i>A</i>	3
2942 vs	2940 vs		2925 <i>B</i>	25
		2940 (40) p	2934 <i>A</i>	2
	2960 s		2929 <i>B</i>	24
3040 vs	3022 vs	3026 (27) p	3050 <i>A</i>	1
3078 w	3065 w	3065 (2) dp	3048 <i>B</i>	23

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Table 3 offers a comparison<sup>14</sup> between the observed spectrum of *cyclohexene* and a zero-order calculated spectrum obtained by adding to the aliphatic field of Snyder and Schachtschneider a set of ethylenic force constants taken from a previous refinement<sup>15</sup> on 1:4-*cyclohexadiene* and the fully deuterated analogue. It is easily seen from the table that not only are the essential features of the observed spectrum reproduced in the calculated one, but also the agreement is extremely satisfactory. Each time there is a polarized line in the Raman spectrum, there is always, within a few wave numbers, a frequency of species *A* in the calculated spectrum, whereas each time a band with a *Q* branch occurs in the IR spectrum, there is always a

Table 4. Comparison between the observed and the zero-order calculated spectrum of *cyclohexene-d*<sub>10</sub>

<i>I.R. (gas)</i>	<i>I.R. (liq.)</i>	<i>Raman (liq.)</i>	<i>Calc.</i>	<i>N</i>
			182 <i>B</i>	42
		230 (2) dp	232 <i>A</i>	22
		327 (3) p	337 <i>A</i>	21
375 m <i>Q</i>	375 m	378 (0.5) dp	384 <i>B</i>	41
		457 (1) dp	472 <i>A</i>	20
497 vs <i>Q</i>	494 vs	497 (0.5) dp	489 <i>B</i>	40
608 m <i>Q</i>	605 m		606 <i>B</i>	39
		618 (0.5) dp	616 <i>A</i>	19
712 m <i>Q</i>	710 m		695 <i>B</i>	38
		727 (8) p	715 <i>A</i>	18
731 m <i>Q</i>	730 s		710 <i>B</i>	37
	739 w	734 (4) p	742 <i>A</i>	17
	772 w		<i>A</i>	20 + 21
		779 (12) p	752 <i>A</i>	16
795 m <i>Q</i>	791 m		749 <i>B</i>	36
		799 (25) p	767 <i>A</i>	15
		845 (7) p	858 <i>A</i>	14
			850 <i>B</i>	35
872 vs <i>Q</i>	868 vs	874 (0.5) dp	885 <i>B</i>	34
		899 (1) dp	885 <i>A</i>	13
917 w	911 m		<i>A</i>	20 × 2
		923 (3) p	922 <i>A</i>	12
961 m <i>Q</i>		962 (1) dp	965 <i>B</i>	33
		998 (1) p	1001 <i>A</i>	11
1052 w	1048 m		1054 <i>B</i>	32
			1051 <i>A</i>	10
1069 m <i>Q</i>	1064 s	1066 (4) dp	1077 <i>B</i>	31
		1079 (1.5) p	1062 <i>A</i>	9
1083 vs <i>Q</i>	1080 s		1088 <i>B</i>	30
			1150 <i>B</i>	29
	1099 w	1103 (1.5) p	1183 <i>A</i>	8
1174 m <i>Q</i>	1170 s	1171 (1) dp	1217 <i>B</i>	28
		1206 (1) dp?	1235 <i>A</i>	7
	1225		<i>B</i>	17 + 40
	1590		<i>B</i>	36 + 15
1630 m	1619 vs	1621 (22) p	1621 <i>A</i>	6
	2044 vw	2039 (1) p	<i>A</i>	7 + 14
		2087 (30) p	2087 <i>A</i>	5
2102 vs <i>Q</i>	2093 vs		2084 <i>B</i>	27
		2105 (22) p	2090 <i>A</i>	4
2110 vs <i>Q</i>	2115 vs		2087 <i>B</i>	26
		2119 (17) p	<i>A</i>	31 × 2
		2140 (30) p	2180 <i>A</i>	3
		2165 (18) p	<i>A</i>	30 × 2
2191 vs <i>Q</i>	2182 vs	2184 (16) dp	2182 <i>B</i>	25
2211 vs <i>Q</i>	2206 vs	2210 (16) dp	2191 <i>B</i>	24
	2229 m	2221 (16) p	2205 <i>A</i>	2
	2263 s	2264 (14) p	2271 <i>A</i>	1
2268 m	2302 w		2260 <i>B</i>	23
		2343 (2.5) p	<i>A</i>	28 × 2 or 6 + 18

*B* fundamental in the calculated spectrum. I wish to point out that there is only one band at  $1403\text{ cm}^{-1}$  which differs appreciably from the experimental one. The same agreement is found for *cyclohexene-d*<sub>10</sub> as shown in *Table 4*. Again there is only one frequency at  $1183\text{ cm}^{-1}$  which differs from the experimental value.

This force field was then refined using the frequencies of both isotopic species and the final force field is shown in *Table 5*. The refined frequencies

*Table 5. Valence force field of cyclohexene*

Description	Values	Description	Values
	$K_l = 5.068$		$F_{\phi D} = 0.365$
	$K_{\sigma} = 4.552$		$F'_{T\gamma} = 0.047$
	$K_D = 8.700$		$F'_{T\varphi} = 0.077$
	$K_R = 4.384$		$F_{R\omega} = 0.423$
	$H_{\epsilon} = 0.917$		$F_{\gamma\gamma} = -0.019$
	$H_{\omega} = 1.051$		$F'_{\gamma\gamma} = 0.019$
	$H_{\delta} = 0.544$		$F_{\phi\psi} = 0.033$
	$H_{\varphi} = 0.504$		$F_{\gamma\omega} = -0.034$
	$H_{\psi} = 0.477$		$F_{\epsilon\phi} = -0.043$
	$H_{\theta} = 0.667$		$F_{\gamma\gamma}(tr) = 0.135$
	$H_{\gamma} = 0.661$		$F_{\gamma\gamma}(g) = -0.007$
	$H_T = 0.221$		$F'_{\gamma\gamma}(tr) = 0.005$
	$\tau_D = 0.222$		$F'_{\gamma\gamma}(g) = 0.025$
	$\tau_T = 0.020$		$F''_{\gamma\gamma}(tr) = 0.011$
	$\tau_R = 0.024$		$F''_{\gamma\gamma}(g) = -0.007$
	$F_{DT} = 0.098$		$F_{\gamma\omega}(tr) = 0.062$
	$F_{RT} = 0.124$		$F_{\gamma\omega}(g) = -0.070$
	$F_{\theta T} = 0.360$		$F_{\omega\omega}(g) = -0.017$
	$F_{\gamma R} = 0.341$		$F_{\phi\phi} = 0.122$
	$F_{\psi T} = 0.319$		$F_{dd} = 0.005$

are shown in the *Table 6* and one can see that the two bands which were out of order before have been convinced to choose a more honest behaviour.

*Table 7* shows an application of the *cyclohexene* field to the prediction of the spectrum and to the analysis of the conformational structure of *cyclo-*

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Table 6. Refined frequencies of *cyclohexene-d<sub>0</sub>* and *cyclohexene-d<sub>10</sub>*

<i>N</i>	<i>ν<sub>obs</sub></i>	<i>ν<sub>calc</sub></i>	<i>P.E.D.</i>	<i>ν<sub>obs</sub></i>	<i>ν<sub>calc</sub></i>	<i>P.E.D.</i>
1	3026	3054	0.99 I	2254	2273	0.94 I
2	2940	2934	0.99 d	2221	2205	0.96 d
3	2916	2924	1.0 d	2140	2179	0.98 d
4	2865	2854	0.99 d	2105	2090	0.97 d
5	2839	2853	0.99 d	2087	2087	0.96 d
6	1656	1656	0.79 D + 0.12 R	1621	1618	0.79 D + 0.16 R
7	1436	1463	0.76 A + 0.22 γ	1206	1200	0.97 R + 0.32 γ + 0.44 γ
8	1353	1440	0.803 + 0.14 γ	1193	1195	0.51 R + 0.25 γ + 0.44 γ
9	1343	1328	0.18 R + 0.21 γ + 0.67 γ	1103	1070	0.11 R + 0.77 ε + 0.14 γ
10	1241	1249	0.21 γ + 0.65 γ	1079	1055	0.77 ε + 0.20 γ
11	1222	1222	0.16 R + 0.21 ε + 0.21 ε + 0.33 γ	998	1001	0.11 R + 0.60 γ
12	1141	1141	0.27 γ + 0.77 γ	921	921	0.65 γ
13	1095	1095	0.7 R + 0.20 γ + 0.13 Γ + 0.31 D	899	892	0.60 γ + 0.27 Γ + 0.34 ε
14	1068	1085	0.38 γ + 0.43 Γ + 0.12 γ	845	842	0.1 R + 0.41 ε + 0.74 γ
15	968	967	0.43 Γ + 0.12 γ	805	805	0.21 γ + 0.18 γ
16	966	967	0.69 R + 0.12 γ + 0.10 D	779	770	0.53 R + 0.18 γ
17	905	905	0.83 R	740	740	0.35 R + 0.26 γ + 0.16 Γ
18	822	813	0.18 R + 0.15 γ + 0.64 γ	727	718	0.23 R + 0.11 γ + 0.22 γ + 0.21 Γ
19	789	791	0.11 ε + 0.36 ω + 0.11 γ	615	626	+ 0.13 D
20	435	507	0.31 Γ + 0.34 D + 0.17 R' + 0.1 R	457	459	0.57 γ + 0.59 γ
21	394	392	0.49 ω + 0.17 D + 0.27 R	327	330	0.50 ω + 0.24 γ
22	281	277		230	225	0.34 Γ + 0.43 D + 0.10 R' + 0.50 R + 0.31 R
23	3067	3053	0.99 I	2302	2265	0.96 I
24	2860	2828	0.99 d	2206	2190	0.97 d
25	2898	2925	0.99 d	2182	2182	0.98 d
26	2882	2853	0.99 d	2115	2087	0.97 d
27	2860	2852	0.99 d	2083	2084	0.97 d
28	1450	1455	0.77 ε + 0.14 γ	1170	1180	0.94 R + 0.20 γ
29	1443	1442	0.79 ε + 0.16 γ	1105	1105	0.18 R + 0.14 ε + 0.50 γ
30	1338	1344	0.19 γ + 0.80 γ	1080	1080	0.1 ω + 0.388 + 0.16 γ
31	1321	1314	0.19 γ + 0.65 γ	1064	1058	0.768 + 0.18 γ
32	1321	1314	0.11 R + 0.11 ε + 0.1 ε + 0.13 γ' + 0.56 γ	1048	1047	0.138 + 0.14 ε + 0.13 ε + 0.10 γ'
33	1265	1269	0.67 R + 0.25 ε + 0.16 γ + 0.18 γ	962	963	0.67 γ
34	1139	1214	0.1 R + 0.39 γ + 0.58 γ	868	881	0.17 ε + 0.22 ω + 0.18 + 0.26 γ
35	1040	1088	0.20 R + 0.13 ε + 0.25 ε + 0.1 γ' + 0.24 γ	852	852	0.73 γ' + 0.19 γ
36	1069	985	0.16 ε + 0.27 ω + 0.13 γ + 0.28 γ	772	772	0.12 ε + 0.26 γ + 0.49 γ
37	917	917	0.21 γ + 0.72 γ	730	706	0.99 γ
38	878	861	0.81 R	710	698	0.21 ε + 0.25 ε + 0.36 R + 0.13 γ
39	721	716	0.14 R + 0.18 ε + 0.37 γ + 0.14 Γ	605	618	0.13 R + 0.21 ε + 0.36 γ
40	643	645	0.66 Γ	497	493	0.70 Γ
41	455	463	0.57 ω + 0.34 γ	377	377	0.46 ω + 0.55 γ
42	175	179	0.24 ω + 0.28 R' + 0.350 R	146	146	0.23 ω + 0.30 R' + 0.36 R

Table 7. Predicted and observed spectrum of cycloheptene: calculations were made for three possible forms of Figure 2

IR	Raman	Chair C <sub>2v</sub>	Boat C <sub>2v</sub>	C <sub>2</sub>	IR	Raman	Chair C <sub>2v</sub>	Boat C <sub>2v</sub>	C <sub>2</sub>
		145 A''	130 B	1209 s	1213 (5) p	1198 A'	1180 A'	1219 A	
		234 A'	247 A	1219 s	1221 (5) p	1228 A'	1235 A'	1254 A	
		266 A'		1230 w		1234 A''	1234 A''	1230 B	
314 w	210 (4) dp	314 A''	307 B		1237 (11) p	1252 A'	1260 A'	1286 A	
330 m	317 (13) dp		357 B			1272 A''	1277 A''	1239 B	
352 s	330 (10) dp	344 A'	326 A		1275 (24) p	1312 A'	1292 A'	1328 A	
	354 (10) p	401 A'	466 A			1301 A''	1291 A''	1320 B	
	421 (2) p	481 A''	1339 vw	1339 vw	1339 (11) p	1327 A'	1326 A'	1347 A	
480 m	470 (4) dp	465 A''	1331 w	1331 w		1335 A''	1337 A''	1342 B	
628 s	483 (3) p	529 A'	1360 w	1360 w		1374 A''	1352 A''	1361 B	
688 vs	691 (6) p	597 A''	1439 vs	1439 vs		1443 A'	1442 A'	1418 A	
		682 A'	690 B	690 B	1442 (40) dp	1446 A''	1445 A''	1427 E	
748 w	751 (40) p	778 A'	766 A	766 A	1453 vs	1451 A'	1454 A'	1426 A	
741 w			768 B	768 B	1448 vs	1454 A''	1465 A''	1467 E	
804 m						1461 A'	1468 A'	1469 A	
827 s	483 (A') + 317 (A'') = 800 (A')	483 (A') + 470 (A'') = 824 (A'')				483 (A') + 1077 (A') = 1550 (A')			
832 vs	832 (2) dp	828 A''	819 B	1655 s	1658 (40) p	1655 A'	1654 A'	1653 A	
860 vw		849 A'	852 A	2838 s		2853 A''	2854 A''	2852 E	
	877 (5) p	874 A'	901 A		2841 (40) p	2852 A'	2852 A'	2853 A	
888 w		894 A''		2850 s		2855 A''	2854 A''	2855 E	
962 vs	964 (5) dp	981 A''	948 B		2855 (40) p	2854 A'	2854 A'	2854 A	
988 vw		983 A'	983 A	2885 m	2887 (35) p	2856 A'	2855 A'	2856 A	
			1004 A	2920 vs		2926 A''	2922 A''	2922 B	
1015 w		990 A''	997 A''			2925 A'	2923 A'	2926 E	
1025 w		1013 A''	1023 A''	1028 B		2928 A'	2929 A'	2926 A	
1041 vw	1046 (17) p	1054 A'	1049 A'	1051 A	2928 (60) p	2928 A''	2930 A''	2932 B	
1072 s	1077 (9) p	1069 A'	1058 A'		2960 m	2932 A'	2932 A'	2929 A	
1110 m	1117 (3) dp	1099 A''	1107 A''	1075 B		3054 A'	3054 A'	3053 B	
				1124 A					
1140 w		1151 A''	1127 A''	1137 B	3020 m	3018 (35) p	3055 A'	3054 A'	3054 A
		1195 A''	1202 A''	1157 B					

heptene. Three possible molecular conformations are predicted for cycloheptene from a conformational analysis: the chair, the boat and a third one with C<sub>2</sub> symmetry (Figure 2). In the table, the spectra corresponding to the three forms, calculated using the cyclohexene field, are compared with the experimental results. The differences between the three calculated spectra are rather small above 1000 cm<sup>-1</sup>, but are significant in the low frequency region. For instance one can easily disregard the C<sub>2</sub> form since in the observed spectrum there are polarized Raman lines at 421, 691, 1077 and 1221 cm<sup>-1</sup> and depolarized lines at 210 and 470 cm<sup>-1</sup> which cannot be explained from the spectrum of the C<sub>2</sub> form. Although the differences between the spectra of the two other forms are less marked, it is still possible to make a final choice. Not only does the spectrum of the boat form not explain the experimental bands at 210 and 421 cm<sup>-1</sup>, but it shows several bands as, for instance, the ones at 234 and 266 cm<sup>-1</sup> for which no counterpart can be found in the observed spectrum. The same force field was extended with success to *cis*-cyclooctene<sup>17</sup> for which two possible configurations, the chair and the boat were considered. In this case too it was again found that only the spectrum calculated for the chair form could be correctly paired to the observed one.

We have pushed the process of transfer further and used the *cis*-cyclohexene field to predict the spectrum of a *trans*-cycloolefin. Happily we had at our

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Cycloheptene

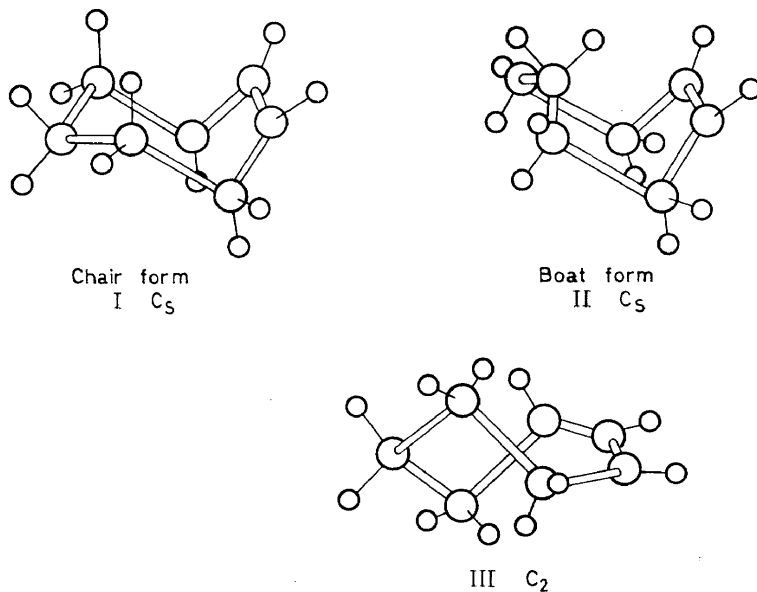


Figure 2

disposal the right molecule, a large cyclenic ring, *t,t,t*-cyclododecatriene (Figure 3) for which an unquestionable vibrational assignment<sup>18</sup> had been worked out. Owing to the difference between *cis* and *trans* ethylenic groups, one expects from the zero-order calculation only a qualitative indication of the location of the fundamentals.

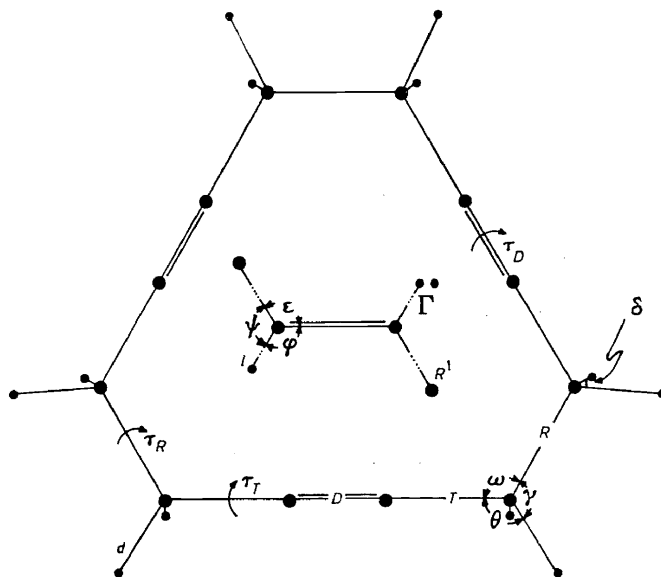


Figure 3

In *Table 8* the calculated zero-order spectrum<sup>19</sup> is compared with the experimental assignment. The agreement is undoubtedly much better than expected. Only very few frequencies actually differ from experiment, others being within a few wavenumbers of the correct value. Moreover all

*Table 8.* Comparison between the observed and the zero-order calculated spectrum of *t,t,t-cyclododecatriene*

IR	Raman	Obs.	Zero-order	IR	Raman	Obs.	Zero-order
135 m	97 (46) dp	29 E 16 A <sub>2</sub>	89 E 137 A <sub>2</sub>		1208 (23) p	8 A <sub>1</sub> 43 E	1209 A <sub>1</sub> 1216 E
	146 (5) dp	30 E	123 E			44 E	1259 E
	174 (6) p	1 A <sub>1</sub>	186 A <sub>1</sub>	1276 s (I)	1282 (3) dp	45 E	1285 E
215 vs	218 (6) dp	31 E	221 E	1302 s (II)		23 A <sub>2</sub>	1305 A <sub>2</sub>
266 s		17 A <sub>2</sub>	273 A <sub>2</sub>		1304 (9) p	9 A <sub>1</sub>	1304 A <sub>1</sub>
	331 (10) p	2 A <sub>1</sub>	322 A <sub>1</sub>		1318 (5) p	10 A <sub>1</sub>	1331 A <sub>1</sub>
350 w		16+31		1330vw (II)			
373 w	375 (0-5) dp	32 E	376 E	1350 vs (II)		24 A <sub>2</sub>	1356 A <sub>2</sub>
448 s (I)	453 (4) dp	33 E	443 E		1351 (4) dp	46 E	1351 E
	482 (9) p	3 A <sub>1</sub>	478 A <sub>1</sub>			47 E	1358 E
		18 A <sub>2</sub>	479 A <sub>2</sub>	1430 vs (II)		25 A <sub>2</sub>	1417 A <sub>2</sub>
511 s (I)		34 E	511 E	1436 vs (I)	1440 (9) dp	48 E	1442 E
710vw (I)		2+32		1445 s (I)		49 E	1455 E
768 w (II)		19 A <sub>2</sub>	755 A <sub>2</sub>		1447 sh p	11 A <sub>1</sub>	1456 A <sub>1</sub>
786 w (I)	779 (5) dp	35 E	812 E	1675 w (I)		50 E	1670 E
	811 (2) p	4 A <sub>1</sub>	802 A <sub>1</sub>		1677 (40) p	12 A <sub>1</sub>	1677 A <sub>1</sub>
855 vs (I)	858 (2) dp	36 E	852 E	2844 s (II)		26 A <sub>2</sub>	2863 A <sub>2</sub>
882vw (II)		20 A <sub>2</sub>	895 A <sub>2</sub>	2844 s (I)		51, 52 E	2854 E
919 w (I)	914 (0-5) dp	37 E	891 E		2848 (40) p	13 A <sub>1</sub>	2855 A <sub>1</sub>
952 vs (I)	955 (3) dp	38 E	912 E	2878 m (I)		48+49	
974 vs (I)	979 (3) dp	39 E	973 E	2912 vs (I)		53 E	2925 E
	993 (3) p	5 A <sub>1</sub>	915 A <sub>1</sub>		2914 (80) p	14 A <sub>1</sub>	2930 A <sub>1</sub>
1017 vs (I)		40 E	990 E	2919 vs (II)		27 A <sub>2</sub>	2925 A <sub>2</sub>
1022 sh (I)		2×34			2934 (30) dp	54 E	2930 E
		6 A <sub>1</sub>	1038 A <sub>1</sub>	2935 vs (II)			
1041 vs (II)		21 A <sub>2</sub>	1033 A <sub>2</sub>	2966 vs (II)			
1095 w (II)		22 A <sub>2</sub>	1091 A <sub>2</sub>	2989 vs (II)			
	1097 (2) dp	41 E	1103 E	3005 s (II)			
1130vw (II)		16+5			3004 (17) p	15 A <sub>1</sub>	3064 A <sub>1</sub>
	1153 (0-5) p	7 A <sub>1</sub>	1153 A <sub>1</sub>	3032 vs (II)		28 A <sub>2</sub>	3045 A <sub>2</sub>
1169vw (II)						55 E	3045 E
1197 vs (I)		42 E	1202 E			56 E	3064 E

frequencies, for which a large deviation occurs, are according to the PED, essentially vibrations of the ethylenic groups. It is evident that the calculated spectrum repeats all features of the observed spectrum. Whenever there is a polarized Raman line there is always a calculated A<sub>1</sub> fundamental, and the same is true for A<sub>2</sub> and E vibrations which are identified from their crystal polarization. *Table 9* shows the refined frequencies<sup>19</sup> and one can see that the agreement is excellent for all vibrations.

In *Table 10* the refined force field is compared with the *cyclohexenic* field. Only two force constants—the torsion around the double bond and the out-of-plane CH deformation—have reached a value which is quite different from the original one. All other force constants are instead only slightly different.

A further application of the *trans*-cyclenic field is shown in *Table 11*, where the calculated spectra of 1:4-*trans*-polybutadiene and of three deuterio-derivatives are compared with the experimental results<sup>20</sup>.

## FORCE FIELD OF LARGE MOLECULES











































 Table 9. Refined frequencies of *t,t,t*-cyclododecatriene

<i>Species</i>	<i>No.</i>	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$	<i>Species</i>	<i>No.</i>	$\nu_{\text{obs}}$	$\nu_{\text{calc}}$
$A_1$	1	174	195	$E$	29	97	90
	2	331	323		30	146	128
	3	482	480		31	218	223
	4	811	812		32	375	378
	5	993	988		33	448	443
	6	—	1044		34	511	523
	7	1153	1153		35	786	786
	8	1208	1206		36	855	855
	9	1304	1297		37	914	897
	10	1318	1322		38	955	966
	11	1447	1447		39	979	993
	12	1677	1678		40	1017	1011
	13	2848	2846		41	1097	1096
	14	2914	2921		42	1197	1197
	15	3004	3027		43	—	1220
$A_2$	16	133	142	44	—	1258	
	17	266	275	45	1282	1286	
	18	—	473	46	1351	1353	
	19	768	767	47	—	1359	
	20	882	892	48	1436	1434	
	21	1041	1034	49	1445	1446	
	22	1095	1097	50	1675	1671	
	23	1302	1302	51	2844	2844	
	24	1350	1348	52	2844	2845	
	25	1430	1432	53	2912	2917	
	26	2844	2844	54	2934	2921	
	27	2919	2916	55	—	3009	
	28	3032	3009	56	—	3027	

Another valence force field of general use is that derived in our laboratory for aromatic molecules<sup>9</sup>. This force field has been applied with success to the prediction of the spectra of phenanthrene<sup>21</sup>, deuterophenanthrene<sup>22</sup> and pyrene<sup>23</sup>.

These examples prove that approximate force fields are useful; are they also unique solutions? Of course they are not, and they cannot be, because of the method by which they are constructed. In fact, how do we proceed in constructing a force field? We build up a model, a model made of point masses and harmonic coupled springs and we expect this model to reproduce, within a given range, a set of vibrational frequencies. The number of models, with the same masses and different springs, which possess vibrational frequencies within that range can be relevant if the range is large and the number of points small. Since there are real difficulties in reducing the range, it is often more convenient to increase the number of points. This is, in simple words, the essence of the overlay technique, by which the same force field is used to refine several molecules all together. In this way the number of possible models is reduced, but there is no guarantee that the solution becomes unique. In *Table 12*, two different force fields of benzene both obtained with an overlay refinement are shown. The first was obtained by us with an overlay refinement of benzene, naphthalene and anthracene<sup>9</sup> and the corresponding deuterio compounds. The second by Scherer<sup>24</sup> with an overlay refinement of benzene and a series of chloro-benzenes. Although the two fields have been obtained using a different series of molecules and different number of force constants, the differences between similar terms of

Table 10. Trans-cyclic field















	$\Phi_0$	$\Phi$		$\Phi_0$	$\Phi$		$\Phi_0$	$\Phi$		$\Phi_0$	$\Phi$
	$K_1$	5.068		$F_{dd}$	0.005	0.004		$F_{\omega^g}$	-0.034	-0.028	
	$K_d$	4.552		$F_{TR}$	0.124	0.122		$F_{\omega^g}$	0.122	0.121	
	$K_0$	8.700		$F_{DT}$	0.098	0.094		$F^{tr}$	0.135	0.120	
	$K_R$	4.384		$F_{Dop}$	0.365	0.355		$F^g$	0.007	0.012	
	$K_T$	1.051		$F_{Tp}$	0.319	0.333		$F^{tr}$	0.005	0.008	
	$H_w$	0.544		$F_{T\theta}$	0.360	0.341		$F^g$	0.025	0.029	
	$H_6$	0.917		$F_{R\gamma}$	0.341	0.348		$F^g$	0.011	0.008	
	$H_t$	0.504		$F_{Tp}$	0.077	0.075		$F^{tr}$	0.007	0.006	
	$H_q$	0.477		$F_{D\omega}$	0.047	0.066		$F^{tr}$	0.062	0.005	
	$H_{tp}$	0.667		$F_{R\theta}$	0.423	0.419		$F_{\omega^g}$	0.070	0.045	
	$H_\theta$	0.661		$F_{De}$	0.019	-0.032		$F_{\omega^g}$	0.081	0.080	
	$H_\gamma$	0.221		$F_{T\omega}$	0.019	0.015		$F_{\omega^g}$	0.017	0.012	
	$H_r$	0.222		$F_{R\omega}$	0.033	0.027		$F_{\omega^g}$	0.029	0.029	
	$T_0$	0.024		$F_{\theta\theta}$	0.043	-0.029		$F_{\omega^g}$	0.017	0.012	
	$T_d$	0.024		$F_{\theta\theta}$	0.043	-0.029		$F_{\omega^g}$	0.017	0.012	
	$T_r$	0.024		$F_{\theta\theta}$	0.043	-0.029		$F_{\omega^g}$	0.017	0.012	
	$T_R$	0.020		$F_{\theta\theta}$	0.043	-0.029		$F_{\omega^g}$	0.017	0.012	

FORCE FIELD OF LARGE MOLECULES

Table 11. Calculated and observed spectra of some polybutadienes

Species	$d_0$		2:3- $d_2$		1:1:4:4- $d_4$		$d_6$	
	$\nu_{obs}$	$\nu_{calc}$	$\nu_{obs}$	$\nu_{calc}$	$\nu_{obs}$	$\nu_{calc}$	$\nu_{obs}$	$\nu_{calc}$
$A_g$	—	3027	—	2923	—	3026	—	2272
	—	2923	—	2848	—	2194	—	2191
	—	2848	—	2270	—	2089	—	2089
	—	1667	—	1640	—	1658	—	1632
	—	1433	—	1432	—	1285	—	1170
	—	1331	—	1317	—	1176	—	1106
	—	1304	—	1298	—	1080	—	1139
	—	1259	—	1138	—	1035	—	976
	—	1141	—	1038	—	974	—	949
	—	1039	—	992	—	916	—	870
	—	962	—	907	—	821	—	786
	—	759	—	664	—	686	—	618
	—	555	—	507	—	498	—	465
	—	223	—	199	—	212	—	186
$A_u$	3018	3009	2920	2914	3000	3009	2207	2217
	2915	2914	2843	2842	2200	2171	2183	2169
	2840	2842	2207	2216	2090	2072	2098	2072
	1453	1426	1455	1426	1240	1214	1095	1125
	1312	1302	1235	1268	1080	1084	1070	1042
	1235	1245	1188	1209	1045	1040	970	957
	1075	1066	1028	1049	970	986	917	909
	1054	1035	845	856	930	916	785	760
	978	986	750	742	—	826	712	712
	773	769	718	714	565	584	588	588
	440	426	—	414	—	389	—	—
	—	301	—	292	—	267	—	—

Table 12. Comparison of two overlay fields of benzene

	$\Delta$				$\Delta$		
	This work	Scherer			This work	Scherer	
	5.055	5.171	0.116		0.174	0.167	0.007
	6.433	6.602	0.169		0.164	0.270	0.106
	0.934	0.924	0.010		-0.045	-0.022	0.023
	0.511	0.508	0.003		—	0.256	—
	0.750	0.770	0.020		—	-0.008	—
	-0.316	-0.371	0.055		0.017	—	—
	0.342	0.367	0.025		—	0.144	—

the force fields are within errors, only one force constant being actually different in the two cases. Once we accept the idea that several solutions exist for the force field of a large molecule, with different numbers and types of force constants, we must do our best to find all these solutions and compare them in detail. For instance I feel, and I am sure that many spectroscopists share this feeling, that one of the reasons for the present situation is that nobody has a clear idea of what should be considered a good frequency fit. As a matter of fact, each one of us has his own standard, which is rigidly applied in judging the work of other people but more flexibly applied when it comes to his own. The consequence is that the range in which calculated frequencies are considered to fit the experimental data, is undefined.

Of course there are objective reasons for it, as for instance the use of crystal or liquid instead of gas frequencies, the indeterminate molecular geometry, the harmonic approximation and so on. Nevertheless I believe that something should be done, at least in the form of a gentlemen's agreement or, even better, through precise indications of the I.U.P.A.C. Committee for Spectroscopy.

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