

Valence Force Fields as a Tool in Vibrational Spectroscopy and Molecular Mechanics

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Force field calculations on conjugated molecules are discussed. The discussion is based on the experience of a series of overlay calculations, recently carried out, where the transferability of force constants was thoroughly studied. Successful applications as well as limitations of the constructed force field are described. The effects of nonbonded interactions are recognized as the most serious restriction of the transferability of valence force fields, and it is suggested that the molecular mechanics method, where the nonbonded interactions are taken explicitly into account, would be advantageous. The treatment of potential energy in the molecular mechanics method is briefly described and the connections between valence force constants and potential energy parameters in this method are discussed.

1. INTRODUCTION

Force field calculations have long been used as a tool in vibrational spectroscopy. For large molecules the best way of deriving a reliable valence force field has proved to be the overlay technique, in which force constants are assumed to be transferable between related molecules, or parts of molecules. But it is well known, too, that force fields for large molecules nevertheless are far from trivial to construct and that considerable care should be taken in the process. However, once obtained, a good force field is of great help in the interpretation of complicated vibrational spectra. On the other hand, there are also cases where the transferability of quadratic valence force fields breaks down and other methods have to be used.

One of the most important reasons for the shortcomings of force field calculations is the effect of nonbonded interactions. These are generally not taken explicitly into account, which sometimes leads to severe nontransferability of force constants. In the molecular mechanics method, which is perhaps best known for its applications in conformational analysis, the non-

bonded interactions are included as part of the overall potential energy function¹⁻⁴. It is clear, then, that if the parameters which pertain to the quadratic part of that function, expressed in terms of valence bonds and angles and including cross terms, could be made as accurate as in successful force field calculations, this would provide a very effective tool *e.g.* for studying vibrations in different conformations and in the solid state. Simultaneously, of course, it would improve the accuracy of molecular mechanics calculations of other molecular properties.

Force constants derived in ordinary force field calculations are usually not quantitatively transferable to molecular mechanics calculations. But, in fact, what is needed is a knowledge about what approximations one can make in the quadratic part of the potential energy function, especially as regards cross terms, and such approximations are easy to investigate with the computationally cheaper spectroscopic force field calculations. However, when using the deduced information it is important to be aware of the uncertainties that inevitably exist in valence force fields.

A project for the construction of accurate potential energy functions to be used in molecular mechanics calculations on molecules and molecular crystals that consist of weakly coupled conjugated systems, and which are too large to be economical to treat by *ab initio* methods, is currently in progress in this laboratory. A molecule is considered to be built up of weakly coupled systems if the structure of its subsystems is not significantly deformed due to conjugation as compared to that of the corresponding individual molecules (if they exist) or parts of related molecules. The aim of the present paper is to discuss the merits, limitations and direct failure of force field calculations on this kind of compounds, and to explain the relation to the more general molecular mechanics method.

2. FORCE FIELD CALCULATIONS ON CONJUGATED MOLECULES

2.1. General

For small molecules that contain only a few atoms, or possess very high symmetry, it is possible to derive individual general valence force fields (GVFF). This can be done either by *ab initio* methods or by optimizing the force field directly on empirical data. Experience has shown that *ab initio* force constants derived as second order derivatives at the minimum of the Born-Oppenheimer potential surface become too large, unless truly extensive basis sets are used. In general, these force constants have to be scaled by utilizing experimental data. The scaling factors are transferable between related molecules so that vibrational frequencies can be predicted⁵ but, unfortunately, the applicability of *ab initio* methods to larger molecules is restricted by the enormous consumption of computer time. However, useful information regarding approximations in force fields for large molecules may be deduced from *ab initio* calculations on smaller related molecules.

When using empirical data for the direct determination of a force field, the picture is very different. For small molecules, the force constants may be optimized on vibrational frequencies, small isotope shifts, Coriolis coupling constants etc.. But for large molecules the only reliable experimental data that exist are the vibrational frequencies, of which there are not enough to allow determination of a complete GVFF. On the other hand, most of the

interaction force constants which in principle could be determined using other kinds of data have a negligible influence on the frequencies⁶. A natural approximation is then to leave those force constants out of the optimization and construct a simplified general valence force field (SGVFF). However, the number of frequencies from one molecule is in most cases still insufficient and the reliability of the force field can be hugely improved by application of the overlay technique. In this method an SGVFF is calculated using frequency data from several different molecules and isotopic species where many force constants are constrained to be equal and varied together in the least squares fit. Correlations between the force constants, which otherwise easily causes ambiguities in their optimized values, are thereby effectively reduced^{6,7}. Although relatively large molecules may be included in an overlay calculation, it appears that a more reliable force field is obtained if the calculations are started with small well-assigned 'model' molecules. In larger, structurally related molecules the intermediate results may then be utilized for checking the assignments.

In conjugated systems it is not obvious which interaction force constants one can neglect and which not. Similarly, other constraints between the force constants have to be carefully tried out in test calculations. It should be realized, however, that in an SGVFF the neglected small interaction force constants become compensated by those present. This means that it is of vital importance for the transferability of the force field that the same approximations are used consistently in every molecule included, even though for small molecules it would be possible to determine more complete individual force fields.

2.2. Coordinates, Redundancies and the PED

The force constants in a valence force field are, by definition, related to a set of internal coordinates which reflect changes in the valence bonds and angles of the molecules. The internal coordinates are not always linearly independent and it is of crucial importance that redundancies among them are correctly handled. This matter sometimes causes confusion and has been thoroughly discussed in the literature⁸⁻¹³. A simple but illuminating example is the redundancy among the three valence angle bending coordinates in planar trigonal systems⁹. The redundancy is due to the evident physical fact that the three angles cannot increase simultaneously. This means that only two independent angle coordinates can be defined. Accordingly, a maximum of three independent force constants (*e.g.* two diagonal and one interaction force constant) which are purely associated with the valence angles can be determined. On the other hand, if all three of the angle bending coordinates are used, the dimension of the force constant matrix increases but the number of independent force constants remains the same. One therefore has to be very careful not to optimize too many force constants independently. This is the greatest problem of redundant coordinates. In the simple trigonal system the redundancy is easily avoided by defining one wagging coordinate and one angle bending coordinate, but in more complicated cases, *e.g.* cyclic redundancies in ring structures, it is far more convenient to use directly a set of dependent coordinates. The number of independent force constants must then be deduced by a group theoretical analysis of the vibrations, based on Car-

tesian coordinates. However, the force field may well be optimized without exact knowledge of the redundancy relations.

The potential energy distribution PED, which gives information about the relative contributions of the force constants to the potential energy of a normal mode, is often restricted to the diagonal terms only. But in the case of conjugated molecules, where many of the interaction force constants are large, it is useful to include also the contributions from the off-diagonal elements. Alternatively, an even better picture of the significance of the individual force constants is obtained by deriving the frequency-changes that correspond to small variations (*e.g.* 10⁰%) in the force constant values. This utility, which is extremely powerful when developing a force field, has been implemented in an upgraded version¹⁴ of the MOLVIB program^{15,16} which we have used in all our force field calculations.

2.3. Determination of the Force Constants

Following the principles outlined above we have, in a recent series of papers,¹⁷⁻²¹ constructed a transferable valence force field for such conjugated compounds, containing carbon, hydrogen and oxygen, that can be considered to consist of weakly coupled systems (*e.g.* *p*-benzoquinone, styrene, ethynylbenzene). Presently the force field comprises 150 independent parameters and about 1400 experimental frequencies from 20 different molecules (65 isotopomers) were used in the optimizations. Full information on the compounds, frequencies and force constants is given in the papers mentioned. The molecules included in the calculations were carefully chosen so that they would provide as reliable a basis as possible for the determination of the force constants of each group. That difficulties still occurred with correlations between the force constants only illustrates the severity of these problems.

It turned out that the force constants associated with the stretching of the 'weak' C—C bonds were particularly difficult to optimize and, to begin with, they had to be estimated from other sources²²⁻²⁴ and kept fixed. They could not be varied until accurate initial values had been obtained for the interaction force constants involved. Fortunately, the stretching (and torsion) force constants depend on the bond lengths which means that in a proper force field their values should lie on a fairly smooth curve. This provides a simple means of checking that the force field is physically reasonable. Figure 1 shows the behaviour of the carbon-carbon stretching and torsion force constants derived in our study.

The force constants for the C≡C—C and C≡C—H linear angle bending in ethynylbenzene and *m*- and *p*-diethynylbenzene were also difficult to determine^{20,21}. Like Baranović *et al.*²⁵, we noticed that it was not possible to optimize these force constants unambiguously using frequency data from the benzene derivatives and their deuteromers only. In fact, it could not even be clarified whether or not the in-plane force constants differ from the out-of-plane force constants. A separate investigation that explicitly addressed this problem was therefore undertaken using small molecules like diacetylene, methylacetylene and vinylacetylene¹⁹. The results showed that the C≡C—C(sp³) and C≡C—C(sp) bending force constants were equal with high accuracy, from which fact it was concluded that the in-plane and the out-of-plane linear bending force constants could be considered to be equal also in the ethynyl

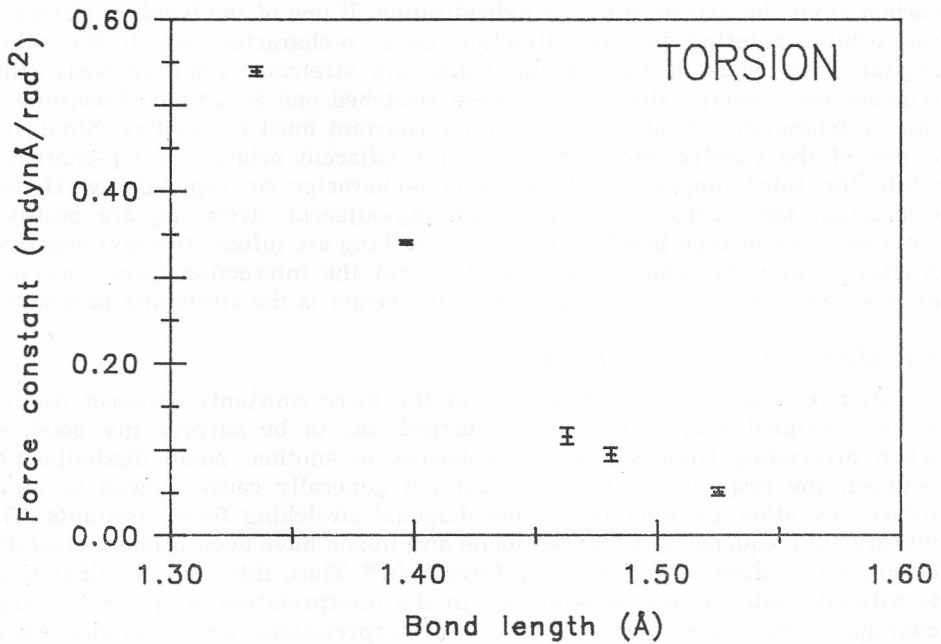
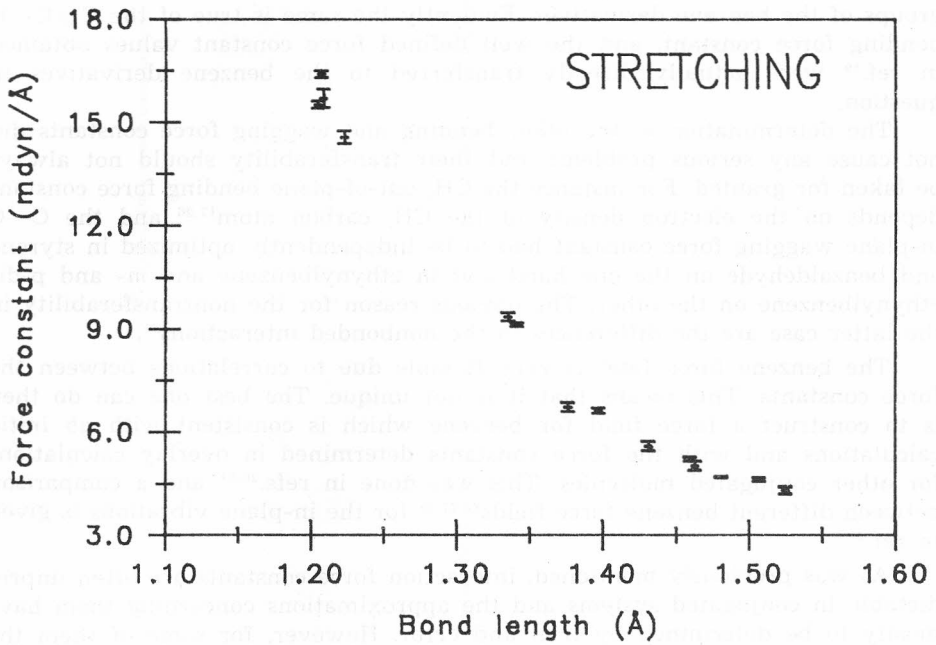


Figure 1. The bond length dependence of the carbon-carbon stretching and torsion force constants derived in our study.

groups of the benzene derivatives. Evidently the same is true of the $C\equiv C-H$ bending force constant, and the well defined force constant values obtained in ref.¹⁹ were actually directly transferred to the benzene derivatives in question.

The determination of the other bending and wagging force constants did not cause any serious problems, but their transferability should not always be taken for granted. For instance the CH_2 out-of-plane bending force constant depends on the electron density of the CH_2 carbon atom^{17,26} and the $C-C$ in-plane wagging force constant had to be independently optimized in styrene and benzaldehyde on the one hand and in ethynylbenzene and *m*- and *p*-diethynylbenzene on the other. The obvious reason for the nontransferability in the latter case are the differences in the nonbonded interactions²¹.

The benzene force field is very flexible due to correlations between the force constants. This means that it is not unique. The best one can do then is to construct a force field for benzene which is consistent with *ab initio* calculations and with the force constants determined in overlay calculations for other conjugated molecules. This was done in refs.^{20,21} and a comparison between different benzene force fields^{25,27,28} for the in-plane vibrations is given in ref.²¹.

As was previously mentioned, interaction force constants are often unpredictable in conjugated systems and the approximations concerning them have mostly to be determined by trial and error. However, for some of them the sign can be checked by applying simple hybridization arguments²⁹. This is the case of adjacent stretching-stretching interactions and the nearest neighbour stretching-bending interactions. Consider *e. g.* a situation with a central carbon atom characterized by sp^2 hybridization. If one of the bonds is stretched the orbital pointing in that direction gains *p*-character, which the other orbitals lose. Thus, if two of the bonds are stretched simultaneously, this requires more energy than if they were stretched one at a time. Accordingly, the stretching-stretching interaction force constant must be positive. Similarly, if one of the valence angles increases, the adjacent orbitals lose *p*-character while the third (opposite) orbital gains *p*-character correspondingly. Hence, interaction force constants of type bending-adjacent stretching are positive, whereas those of type bending-opposite stretching are (often strongly) negative. Another regularity which was noticed is that the interaction force constants of this kind tend to have a larger value the larger is the stretching parameter.

2.4. Merits of the Force Field

In most cases the transferability of the force constants obtained for the weakly coupled conjugated systems turned out to be surprisingly good, so when proceeding from one set of molecules to another, small dissimilarities between the respective subsystems did not generally cause a need to reoptimize any other parameters but the diagonal stretching force constants. The vibrational frequencies of *trans*-stilbene and tolane have even been successfully calculated by direct transfer of the force field³⁰. Thus, this kind of calculations is without doubt an indispensable aid in the interpretation of spectra of large conjugated molecules where serious misinterpretations are otherwise easily made because of Fermi resonance, low-intensity modes, overlapping bands, wrongly estimated group frequencies, *etc.*

2.4.1. Explanation of Unexpected Spectral Features

Our calculations have revealed that the normal modes sometimes change unexpectedly on isotopic substitution and that also the Raman or IR intensity patterns may change considerably. *trans*-Stilbene³⁰⁻³³ exhibits some interesting examples of this.

In the 1600 cm^{-1} region of the Raman spectrum of *trans*-stilbene three fundamentals should be located for which it is a priori clear that the corresponding normal modes mainly involve the C=C stretching and the ring stretching coordinates. The normal coordinate analysis³⁰ showed that the C=C stretching is clearly predominant in one of these modes, this being the case also in nearly all the deuteromers studied. However, in *trans*-stilbene- d_2 there is no distinct C=C stretching and ring stretching. The PEDs of these modes in *trans*-stilbene- h_{12} , $-d_{12}$, $-a, a'-d_2$ and $-a-d_1$ are given in Table I together with the observed and calculated frequencies. Experimentally³¹, two

TABLE I

The Raman active C=C stretching and ring stretching modes in the 1600 cm^{-1} region of *trans*-stilbene- h_{12} , $-d_{12}$, $a, a'-d_2$ and $a-d_1$. The observed and calculated frequencies are in units of cm^{-1} . The PEDs are given in terms of the force constants and include only diagonal contributions of at least 10%. For the sake of simplicity the force constants are denoted by the corresponding coordinates³⁰: R_s (C=C stretching), R_b (ring stretching), R_w (C—C stretching), β_b (ring C—H wagging), β_v (vinyl C—H wagging), α_s (C=C—C bending) and α_b (ring angle bending)

	obs	calc	Δ	PED			
<i>trans</i> -stilbene- h_{12}							
a_g							
	1639	1629	-10	$R_s(72)$	$R_w(21)$	$\beta_v(17)$	$R_b(11)$
	1594	1604	+10	$R_b(70)$	$\beta_b(24)$	$\alpha_b(11)$	
	1572	1586	+14	$R_b(77)$	$\beta_b(23)$	$\alpha_b(11)$	
<i>trans</i> -stilbene- d_{12}							
a_g							
	1596	1604	+8	$R_s(76)$	$R_w(25)$	$\beta_v(12)$	
	1555	1561	+6	$R_b(81)$	$\beta_b(13)$	$\alpha_b(11)$	
	1535	1543	+8	$R_b(88)$	$\alpha_b(10)$		
<i>trans</i> -stilbene- $a, a'-d_2$							
a_g							
	1607	1615	+8	$R_b(44)$	$R_s(32)$	$R_w(19)$	$\beta_b(16)$
	1590	1594	+4	$R_s(44)$	$R_b(40)$	$\beta_b(12)$	
	1568	1586	+18	$R_b(74)$	$\beta_b(23)$	$\alpha_b(10)$	
<i>trans</i> -stilbene- $a-d_1$							
a'							
	1618	1621	+3	$R_s(56)$	$R_b(23)$	$R_w(22)$	$\beta_v(11)$
	1593	1608	+15	$R_b(75)$	$\beta_b(27)$	$\alpha_b(13)$	
	1593	1601	+8	$R_b(59)$	$R_s(23)$	$\beta_b(20)$	
	1570	1586	+16	$R_b(78)$	$\beta_b(23)$	$\alpha_b(11)$	
	1570	1586	+16	$R_b(77)$	$\beta_b(23)$	$\alpha_b(11)$	

of the lines observed near 1600 cm^{-1} are strong in the Raman spectra of those isotopomers for which the modes are distinct, whereas in the case of α,α' -*trans*-stilbene- d_2 only one strong line is found. Using a force field optimized directly on frequencies from *trans*-stilbene and benzene and several deuteromers Meić *et al.*³³ have also reported differing mode structure in α,α' -*trans*-stilbene- d_2 , although their calculated PEDs are different from ours because of different approximations in the force field.

Another interesting case of changed intensity pattern on isotopic substitution was noticed by Gustafson *et al.*³² when they measured and compared the Raman spectra of *trans*-stilbene and α,α' - ^{13}C substituted *trans*-stilbene. Instead of the expected modest deviations in the band positions, surprisingly large changes of the spectral features were observed in the 1600 cm^{-1} and 1300 cm^{-1} regions. According to our normal coordinate analysis³⁰, however, the main reason for this is not extensive mode changes but an exchange of the mutual order of the Raman bands corresponding to some of the modes in question. In the 1600 cm^{-1} region the effect is entirely due to a 76 cm^{-1} downward frequency shift of the C=C stretching vibration, but in the 1300 cm^{-1} region, where there is a significant mode change, there is also a rather strong combination or overtone line (in ^{13}C -*trans*-stilbene) that in addition to the frequency shifts contribute to the different appearances of the two Raman spectra^{30,32}. The PEDs of the modes concerned are compared in Table II and the observed and calculated ^{13}C -shifts are shown in Table III. It is worth emphasizing that no isotope shifts (large or small) have been explicitly used

TABLE II

The modes in the $1300\text{--}1600\text{ cm}^{-1}$ region of *trans*-stilbene and α,α' - ^{13}C -*trans*-stilbene. The PED is defined as in Table I

obs	calc	Δ	PED			
<i>α,α'-^{13}C-trans-stilbene</i>						
a_g						
1592	1608	+16	R _b (73)	β_b (26)	α_b (12)	
1580	1590	+10	R _b (74)	β_b (20)	α_b (10)	
1565	1565	0	R _v (70)	β_v (16)	R _w (15)	R _b (12)
1492	1493	+1	β_b (64)	R _b (34)		
1445	1447	+2	β_b (57)	R _b (37)		
1338	1330	-8	β_b (85)			
1306	1305	-1	R _b (98)	β_v (25)	β_b (14)	
1296	1284	-12	R _b (50)	β_v (32)	α_s (11)	R _s (11) β_b (11)
<i>trans-stilbene-h_{12}</i>						
a_g						
1639	1629	-10	R _s (72)	R _w (21)	β_v (17)	R _b (11)
1594	1604	+10	R _b (70)	β_b (24)	α_b (11)	
1572	1586	+14	R _b (77)	β_b (23)	α_b (11)	
1491	1494	+3	β_b (65)	R _b (35)		
1445	1449	+4	β_b (58)	R _b (38)		
1339	1332	-7	β_b (79)			
1327	1310	-17	R _b (37)	β_v (45)	β_b (12)	
1292	1295	+3	R _b (111)	β_b (20)		

TABLE III

The observed and calculated ^{13}C -shifts in trans-stilbene. Only those shifts which are at least 1 cm^{-1} have been included

obs(^{12}C)	obs(^{13}C)	obs. shift	calc. shift
642	639	-3	-3
868	855	-13	-14
1194	1189	5	1
1292	1306	14	10
1329	1296	-33	-26*
1340	1338	-2	-2
1447	1445	-2	-2
1493	1492	-1	-1
1570	1580	10	4
1595	1592	-3	4
1641	1565	-76	-64

* The modes are dissimilar in ^{12}C - and ^{13}C -trans-stilbene.

TABLE IV

Bond lengths and stretching force constants for the $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$ and $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^2)$ bonds treated in our study. Bond lengths marked with an asterisk(*) are assumed ones. For a discussion of the bond length marked with two asterisks (**), see text. The abbreviations for the molecules are: MA = methylacetylene, DMA = dimethylacetylene, EB = ethynylbenzene, DEB = diethynylbenzene, VA = vinylacetylene, DVA = divinylacetylene, DA = diacetylene, DMDA = dimethyldiacetylene, DAX = monohalogenated diacetylene, E = ethene, S = styrene, B = butadiene, A = acrolein, Q = p-benzoquinone and G = glyoxal

	r (Å)	F (mdyn/Å)	Molecule
$\text{C}\equiv\text{C}$	1.2073	16.41 (11)	MA, DMA
	1.2086*	15.91 (05)	EB, DEB's
	1.2086	15.70 (27)	VA, DVA
	1.205**	15.52 (10)	DA, DMDA, DAX
	1.223	14.56 (18)	DAX ($\text{C}\equiv\text{CX}$)
$\text{C}=\text{C}$	1.335	9.36 (12)	E
	1.341*	9.28 (07)	S
	1.341	9.12 (05)	B, A
	1.342	9.12 (05)	VA, DVA
	1.344	9.12 (05)	Q
$\text{C}-\text{C}$	1.463	5.02 (13)	B
	1.463*	4.70 (11)	S
	1.481	4.68 (02)	Q
	1.482	4.68 (02)	A
	1.525	4.30 (11)	G

in the optimization of the force field. The utilization of small shifts is even beyond the scope of an SGVFF for large molecules, since those interaction force constants which significantly affect only the shifts and not the absolute frequencies, are neglected. On the other hand, the first order perturbation treatment used for calculating small shifts cannot be applied when appreciable changes of the normal modes are involved, which is often the case for large shifts.

2.4.2. Estimation of Bond Lengths

For most large conjugated molecules the bond lengths are not accurately known and in force field calculations assumed values have to be used. However, since the calculated vibrational frequencies are more sensitive to the force constants than to the assumed geometry, conclusions concerning relative differences in the bond lengths may still be drawn from the optimized values of the corresponding diagonal stretching force constants. A necessary condition for this is, though, that all the associated interaction force constants are transferred without reoptimization. In this context it should also be noted that no conclusions can be made by comparing stretching force constants from different force fields where different approximations have been made. The stretching force constants and the corresponding reported or assumed bond lengths for some $C\equiv C$, $C=C$, and $C(sp^2)-C(sp^2)$ bonds are given in Table 4 in decreasing force constant order³⁴.

As regards the $C\equiv C$ bonds the smallest bond length (1.205 Å) is reported for diacetylene (DA)³⁵. But this value is obviously too small since the conjugation increases the $C\equiv C$ bond length which in diacetylene, therefore, must be longer than in methylacetylene (MA), as indicated by the force constants.

There are only small differences in the $C=C$ bond lengths and stretching force constants. However, it appears that the force constant for styrene is slightly larger than for butadiene (from which molecule the initial value was taken), indicating that the conjugation is smaller in styrene than in butadiene. This is also in agreement with the $C-C$ stretching force constants and we may conclude that in styrene the $C=C$ bond is slightly shorter and the $C-C$ bond slightly longer than in butadiene.

Conclusions concerning the bond lengths may also be based on the torsion force constants. Especially as regards the $C-C$ bonds comparisons are easy to make because the low-frequency modes are almost pure $C-C$ torsion modes. For glyoxal, *ab initio* calculations by Bock et al.^{22,24} suggested that the $C-C$ bond length would be 1.498 Å or 1.490 Å (two different basis sets), while an electron diffraction study by Kuchitsu et al.³⁶ gave 1.525 Å. Our torsion force constants supported the experimental value since either of the smaller values would have meant a turning point on the force constant-bond length curve (cf. Figure 1). The question must now be considered settled, however, because in a more extensive *ab initio* study Saebø³⁷ obtained 1.527 Å for this $C-C$ bond.

2.5. Limitations of the Force Field

Like any SGVFF our force field for the weakly coupled conjugated systems is an approximation in many respects. This is seen partly as a limitation in the accuracy of the force constants and partly as restricted transferability. We may speak of the former when the calculated frequencies deviate $< 20\text{ cm}^{-1}$ from the observed ones whereas systematic deviations that are much larger than 20 cm^{-1} must be referred to as originating from the latter. Among the features that merely affect the accuracy of the calculated frequencies, without seriously violating the transferability, the following are the most important ones:

- Many interaction force constants have been neglected. In the molecules which formed the basis for the overlay calculations their effect on the frequencies is insignificant, but vibrations may exist in other molecules that are more sensitive to them.
- Interaction force constants representing different local geometries and structure have been combined in order to reduce the effect of correlations. For instance in ref. [18] the difference between C=C and C=O stretching and between C—C=C and C—C=O angle bending was neglected in some of the interaction force constants.
- Many of the frequencies used in the optimizations are from solid or liquid state spectra. Such frequencies are sometimes shifted by intermolecular interactions which may have caused a small distortion of the force field.
- No corrections for anharmonicity have been made. This means that all the force constants collectively account for the anharmonicity.
- Fermi resonance has not been generally taken into account in the calculations.

These are natural uncertainty sources which cause frequency deviations of $< 10 \text{ cm}^{-1}$ on the average^{38,39}. Since there is very little one can do about them they actually set the limit for the accuracy or 'resolution' of an SGVFF for large molecules.

The most important limitation of the force field, however, is the restricted ability to cope with nonbonded interactions. These have not been taken explicitly into account which means that they cause crude errors (nontransferability) in cases where their influence is considerable (*e.g.* in strained molecules) and the geometry is different from what it was in the molecules where the force constants were optimized. By this we have in fact reached the limit of applicability of transferable valence force fields. Note that even if the subsystems in a conjugated molecule retain their structure with respect to the conjugation, *i.e.* they remain weakly coupled, the nonbonded interactions may cause appreciable changes in the force constant values. One example of this, concerning the C—C in-plane wagging force constant in some benzene derivatives, was already mentioned. The 'weak' C—C torsion vibration in styrene constitutes an even more serious case. It turned out, namely, that the C—C torsion force constant is absolutely nontransferable from butadiene to styrene even though the corresponding force constant of acrolein is transferable to benzaldehyde²⁰.

Sometimes the problems of nonbonded interactions can be overcome simply by taking the most important ones into account as extra force constants. This method was successfully applied by Klæboe *et al.*⁴⁰ in their study of 2-(chloromethyl)-2-methyl-1,3-dichloropropane where they explicitly included the nearest Cl...H interaction. Total neglect of the nonbonded interactions would have increased the CCl bending force constant from the normal value of about $1 \text{ m dyn \AA rad}^{-2}$ to $1.5 \text{ m dyn \AA rad}^{-2}$ and would have changed other force constants as well, thus making the force field highly nontransferable. However, this way of treating nonbonded interactions is in general not applicable to large molecules as the nonbonded interactions depend strongly on

the distance between the interacting atoms, which in most cases is not accurately known.

There is really no good general solution to these problems within the frames of conventional force field calculations. Instead, the best way to account for the nonbonded interactions is to include them explicitly as distance dependent functions in the expression for the potential energy, and calculate the frequencies by the molecular mechanics method.

3. VIBRATIONAL SPECTROSCOPY AND MOLECULAR MECHANICS

In the molecular mechanics method¹⁻⁴, which is generally used for calculating conformational properties of large organic molecules, the treatment of the potential energy differs radically from that in spectroscopic force field calculations, although many basic ideas are borrowed from the latter. Vibrational frequencies can also be calculated in the molecular mechanics method. This has been done in particular by Lifson and coworkers⁴¹⁻⁴⁵ who call the method the consistent force field (CFF) method, indicating that both molecular structure and vibrational frequencies are calculated using the same potential energy function. In the following we briefly discuss how potential energy is treated in the molecular mechanics method and the connections to force fields in vibrational spectroscopy³⁴.

In the molecular mechanics approach the potential energy is not a Taylor expansion to the second order around the equilibrium geometry of an individual molecule, as in spectroscopic force field calculations, and the validity of the potential is not restricted to small deviations from the minimum. Instead the potential energy is assumed to consist of the following parts¹⁻⁴:

- Quadratic terms (including cross terms) that describe the distortion of valence coordinates from their "natural values". The harmonicity is not a necessary condition, however, and some quadratic terms may be replaced *e. g.* by Morse potentials.
- Torsion potential functions of cosine type (V_{tor}).
- Nonbonded atom-atom interactions (v_{nb}).

The potential energy is thus given by

$$\begin{aligned}
 V = & \frac{1}{2} \sum F_i (q_i - q_{i0})^2 + \sum_{i < j} f_{ij} (q_i - q_{i0}) (q_j - q_{j0}) + \\
 & + \frac{1}{2} \sum V_{\text{tor}} + \sum v_{\text{nb}}(r_{kl})
 \end{aligned}
 \tag{1}$$

where q_{i0} is the "natural value" the internal coordinate q_i would have without any other coordinates or interactions involved. Note that q_{i0} is not exactly the equilibrium value of q_i in any real molecule, but merely a parameter in the potential energy function common to certain types of coordinates in all molecules. Parameters F_i and f_{ij} have the same dimensions as force constants in conventional force fields but their values are usually different. The nonbonded interactions (v_{nb}) are generally given as Lennard-Jones (12-6 or 9-6) or Buckingham potentials.

The equilibrium geometry of a molecule is found by minimizing the potential energy in Cartesian coordinates. If the Newton-Raphson method is used in the last stage of the minimization, the Hessian matrix in the minimum becomes the force constant matrix in Cartesian coordinates. The vibrational frequencies in the harmonic approximation are thus readily calculated⁴¹.

To discuss the connections between force constants in spectroscopic force fields and the parameters F_i and f_{ij} in eq. (1) we have to look closer at the Hessian matrix. The elements of this matrix are the second order derivatives of the potential energy with respect to the Cartesian coordinates. For a general quadratic term g_{ij} (*i. e.* any term included in the first two sums of eq. (1)) that describe the contributions to the potential energy from the interaction of the internal coordinates q_i and q_j ($i \neq j$) or the contribution from the internal coordinate q_i ($i = j$), the second derivatives are

$$\begin{aligned} \left(\frac{\partial^2 g_{ij}}{\partial x_{k\alpha} \partial x_{l\beta}} \right) = & f_{ij} \left\{ \left(\frac{\partial q_i}{\partial x_{k\alpha}} \right) \left(\frac{\partial q_j}{\partial x_{l\beta}} \right) + \left(\frac{\partial q_i}{\partial x_{l\beta}} \right) \left(\frac{\partial q_j}{\partial x_{k\alpha}} \right) \right. \\ & \left. + \left(\frac{\partial^2 q_i}{\partial x_{k\alpha} \partial x_{l\beta}} \right) (q_j - q_{j0}) + \left(\frac{\partial^2 q_j}{\partial x_{k\alpha} \partial x_{l\beta}} \right) (q_i - q_{i0}) \right\} \end{aligned} \quad (2)$$

where k and l denote atoms and $\alpha, \beta = 1, 2, 3$. For the nonbonded interactions the second derivatives are

$$\begin{aligned} \left(\frac{\partial^2 v_{nb}(r_{ij})}{\partial x_{k\alpha} \partial x_{l\beta}} \right) = & \left(\frac{\partial^2 v_{nb}(r_{ij})}{\partial r_{ij}^2} \right) \left(\frac{\partial r_{ij}}{\partial x_{k\alpha}} \right) \left(\frac{\partial r_{ij}}{\partial x_{l\beta}} \right) \\ & + \left(\frac{\partial v_{nb}(r_{ij})}{\partial r_{ij}} \right) \left(\frac{\partial^2 r_{ij}}{\partial x_{k\alpha} \partial x_{l\beta}} \right) \end{aligned} \quad (3)$$

From these equations it is evident that if there is only little steric strain in the molecule, so that the contribution from the nonbonded interactions is small and the internal coordinates have values close to their "natural values", then only those terms that contain first order derivatives of the internal coordinates contribute significantly to the elements of the Hessian matrix. In this case most of the force constants from the spectroscopic force field can be transferred as initial values for the corresponding potential parameters in the molecular mechanics method. Obviously, the parameters have to be reoptimized because of the nonbonded interactions, but this can mostly be done using the vibrational frequencies of the same molecules that were used when deriving the spectroscopic force field. For instance, even in benzene the effect of the nonbonded interactions on the frequencies is in most cases only a few wavenumbers, although there are some in-plane frequencies where the effect is as large as 40 cm^{-1} ⁴⁶. There are also cases where the effect is quite dramatic. The previously mentioned low frequency torsion in styrene is a good example. The frequency changes from 115 cm^{-1} (torsion force constant from butadiene) to imaginary (negative eigenvalue) when the nonbonded interactions are added. As nonbonded potentials those given by Ermer and Lifson were used⁴⁴. In this estimation no energy minimization was performed, so that the frequency changes were entirely due to the nonbonded interactions

(and not to changes in the geometry). In real calculations the potential energy is, of course, always minimized before the frequencies are derived. It is interesting to note that even the out-of-plane frequencies of a planar molecule are affected by nonbonded interactions. This is due to the second term in eq. (3), as in this case the first term is zero.

4. CONCLUDING REMARKS

In this paper we have discussed the applications of force field calculations to conjugated molecules, and pointed out the finite accuracy of the calculated frequencies and the limited transferability of some of the force constants. Referring to the effects of nonbonded interactions it is clear that the molecular mechanics method is attractive as an alternative tool in vibrational analysis, since with cross terms as well as nonbonded interactions taken properly into account the accuracy of the calculated frequencies should be as good as in conventional force field calculations, and the transferability of the potential energy parameters ought to be even better. A fact we wish to stress is that the inclusion of cross terms is greatly facilitated by utilizing the extensive knowledge about interaction force constants, and approximations concerning them, which can be obtained in spectroscopic force field calculations.

The main interest when using the molecular mechanics method is in many cases not the force field or the vibrational frequencies themselves, but molecular structure and conformational equilibria, and such properties can be calculated reasonably well without cross terms. However, by calculating the frequencies in different equilibria, conformation-sensitive vibrations may be predicted, which can be used as an aid when trying to identify the conformations spectroscopically. Further, in the molecular mechanics method it is relatively easy to take intermolecular forces into account. This can be done simply by including them as atom-atom potentials in the nonbonded terms. Molecular crystals may then be studied without assuming any part of the molecule to be rigid. For instance, vibrational frequencies may be calculated both for the free molecule and the crystal using the same molecular potential energy function so that crystal effects on the vibrations are revealed.

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SAŽETAK

Valentna polja sila kao sredstvo vibracijske spektroskopije i molekulske mehanike

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Raspravljaju se proračuni polja sila konjugiranih molekula. Diskusija se temelji na iskustvu nedavno provedenog niza proračuna prijenosa polja, gdje je temeljito proučena prenosivost konstanti sila. Opisane su uspjele primjene, kao i ograničenja konstruiranog polja sila. Efekti neveznih interakcija utvrđeni su kao najozbiljnije ograničenje prenosivosti valentnih polja sila, te se preporučuje primjena metode molekulske mehanike, u kojoj se nevezne interakcije eksplicitno uzimaju u obzir. Ukratko se opisuje postupak s potencijalnom energijom u metodi molekulske mehanike, te razmatraju povezanosti među valentnim konstantama sila i parametrima potencijalne energije.