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The Carbonyl Stretching Force Constant

II. A Normal Coordinate Treatment

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A normal-coordinate analysis is performed for a series of carbonyl compounds with the purpose of deriving carbonyl stretching force constants. The force constants obtained are too inaccurate to be interrelated, however, and this result is analysed and discussed relative to earlier work.

1. INTRODUCTION

In a preceding paper [1] (hereafter referred to as I) the carbonyl stretching force constants of a series of molecules were predicted by means of a specific version of the Pariser-Parr-Pople SCF approximation. The treatment was partly based on a theoretical analysis originally developed and applied to a set of molecules by Bratož and Besnaïnou.[2]

Observed vibrational frequencies are necessary in order to test predicted force constants by experiment. The carbonyl stretching frequency is one of the most characteristic bond frequencies of organic compounds. The fairly small variations of its magnitude when different molecules are compared, have been ascribed partly to variations in the carbonyl stretching force constant and partly to differences in vibrational coupling to the rest of the molecule.

Bratož and Besnaïnou [3] developed a treatment for separating the effects of the two factors mentioned on the carbonyl stretching frequencies of a series of molecules. They used a simplified type of normal-coordinate analysis in which only diagonal valence force fields were applied and the secular equations were solved by a perturbation method. The carbonyl stretching force constants were adjusted to give agreement between calculated and observed carbonyl frequencies, whereas the remaining force constants were estimated from the literature and kept unchanged. Other observed frequencies were not

considered. In a later paper [2] the results obtained were compared with corresponding values predicted from MO theory.

The present work represents another attempt to derive carbonyl stretching force constants for a series of molecules from observed vibrational frequencies, using normal-coordinate analysis. These force constants would serve as a useful basis for comparison with the MO estimates presented in paper I. The secular equations were solved exactly and several attempts were made to use complete sets of observed fundamental frequencies for adjusting the force fields. The approximation of diagonal valence force fields was applied except for a few cases where one or two selected interaction constants were introduced.

2. THEORY

The theory of molecular vibrations is treated in detail in standard textbooks,[4,5] hence only a few points of particular relevance to the present work will be stressed in this section.

The vibrations of a molecule may be described by any appropriate and complete set of linearly independent internal coordinates. Within the approximation of harmonic vibrations the molecular potential function V is completely defined by the force constant matrix or force field, which is given by its elements, the force constants:

$$F_{ij} = \frac{\partial^2 V}{\partial S_i \partial S_j} \tag{1}$$

S_i and S_j are members of the set of internal coordinates chosen in each particular case.

The purpose of the present work is to derive a set of carbonyl stretching force constants that are sufficiently accurate, at least on a relative basis, to be mutually compared. A way to do this would be to derive force fields for the molecules in question from observed vibrational frequencies and to pick one diagonal element from each matrix.

There are some serious complications connected with this procedure, however. In the first place it is a well known fact that for most molecules the number of independent force constants is much higher than the number of fundamental frequencies, particularly if only one isotopic species is considered. This implies that an infinite variety of force fields all may reproduce the same set of observed frequencies. Unfortunately, the carbonyl stretching force constant may vary considerably within such a set of force fields.

The second complication has to do with the linear independence of internal coordinates. Bond distances and valence angles are well suited as internal coordinates, but all of them often cannot be incorporated in a linearly independent set. This reduces the possibility for carrying force constants over from one molecule to another, and the physical interpretation of certain force constants is confused. The partial derivative in (1) may have completely different meanings, depending on the choice of the remaining internal coordinates, not entering (1).

A possible way out of these two difficulties would be to use some kind of simplified force field combined with rules for carrying force constants over from one molecule to another. A common first approximation is to assume a diagonal valence force field for each molecule. However, as discussed above, the carrying over of many force constants is effectively prevented. Furthermore, if a force field is diagonal when it is based on one set of valence coordinates, it is not necessarily diagonal when based on another set.

These theoretical considerations indicate that accurate force fields cannot be obtained for our series of molecules, and that it is rather doubtful whether it is possible to construct simplified force fields giving the desired force constants.

3. RESULTS AND DISCUSSION

The present calculations include the following molecules: formaldehyde, glyoxal, acrolein, acetaldehyde, acetone, *p*-benzoquinone, and *o*-benzoquinone. The results obtained for three of them are presented in some detail. The symmetry valence coordinates used to describe the vibrations are defined in Fig. 1 and in Table 1.

The following geometrical parameters were assumed: The valence angles of the planar parts of all molecules were set equal to 120° and the angles

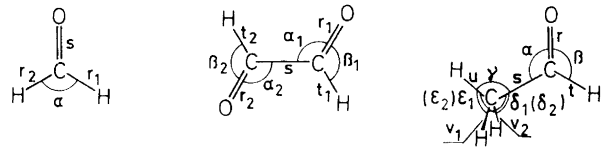

Fig. 1. Labelling of bond lengths and valence angles used to construct the valence symmetry coordinates of formaldehyde, glyoxal and acetaldehyde.

Table 1. Symmetry valence coordinates. The labelling of bond lengths and valence angles is taken from Fig. 1. Normalization constants are omitted.

	Formaldehyde	Glyoxal	Acetaldehyde
Symmetry	C_{2v}	C_{2h}	C_s
Species included	A_1	A_g+B_u	A'
Number of vibr.	3	5 4	10
S_1	r_1+r_2	r_1+r_2	r
S_2	s	s	s
S_3	α	t_1+t_2	t
S_4		$\alpha_1+\alpha_2$	u
S_5		$\beta_1+\beta_2$	v_1+v_2
S_6		r_1-r_2	α
S_7		t_1-t_2	β
S_8		$\alpha_1-\alpha_2$	γ
S_9		$\beta_1-\beta_2$	$\delta_1+\delta_2$
S_{10}			$\varepsilon_1+\varepsilon_2$

around the methyl carbon were assumed tetrahedral. The C=O and C—H bond lengths were set equal to 1.22 Å and 1.09 Å, respectively. The remaining bond lengths are those assumed in a previous article.[6]

The Tables 2—4 present the frequencies resulting from a series of normal-coordinate calculations on three of the molecules. Each calculation started from a force field also given in the tables. The interaction (*i.e.* non diagonal) constants not listed were all set equal to zero. Where diagonal force constants are omitted from the tables they are given in the text. Experimental frequencies are given for comparison. Whereas the indices of force constants correspond to the internal coordinates of Table 1, all frequencies belonging to the same symmetry species of a molecule are numbered consecutively, beginning with the highest.

a) Formaldehyde. This molecule belongs to the point group C_{2v}. Only three of its six normal vibrations are included in the calculations, namely those belonging to the species A_1.

Table 2. Input force fields and resulting frequencies from a series of calculations on the A_1 vibrations of formaldehyde. Observed frequencies are given for comparison. Force constants are given in md/Å and frequencies in cm^{-1}. $F_{12}=F_{13}=0$ in all calculations.

	F_{11}	F_{22}	F_{23}	F_{33}	ν_1	ν_2	ν_3
1. calculation	4.3	12.00	0.37	1.2	2770	1746	1487
2. »	4.3	12.00	0	1.2	2773	1831	1423
3. »	4.3	12.00	0	0.78	2770	1746	1204
4. »	4.3	11.34	0	1.0	2769	1746	1325
5. »	4.3	10.82	0	1.1	2768	1746	1358
6. »	4.3	9.99	0	1.2	2767	1746	1364
7. »	4.3	8.47	0	1.3	2764	1746	1308
Observed [7]					2766	1746	1501

As shown in Table 2, the first calculation gave a good agreement with the observed frequencies.[7] The force field, containing only one interaction constant, was chosen fairly close to the one recently presented in an investigation [8] on several molecules including H_2CO and D_2CO.

When the force field was made diagonal by omitting the interaction constant, the agreement with observed frequencies was destroyed, as demonstrated by the second calculation. The remaining calculations represent an attempt to restore the agreement by adjusting the diagonal force field. This step was necessary as a basis for the comparative treatment of all the molecules. The carbonyl stretching force constant F_{22} and the hydrogen bending force constant F_{33} were varied in a manner leaving the frequency ν_2 constant and equal to the observed value. In this way F_{22} was varied through a total range of 3.5 md/Å. It is seen from the table that within this approach ν_2 and ν_3 cannot be brought to agreement with experiment simultaneously by any diagonal force field since ν_3 has a maximum of about 1370 cm^{-1} when ν_2 is kept equal to the observed value. The results given demonstrate very clearly

that a diagonal force field is not well suited to define and calculate any "best" value of the carbonyl stretching force constant of this molecule.

As discussed earlier, for most molecules an infinite number of valence force fields may fit a given set of frequencies. However, when the force field is assumed diagonal, no exact agreement is possible in the case of formaldehyde. This additional complication was also true for the remaining molecules, as will be shown.

Table 3. Force fields (md/Å) and resulting frequencies (cm^{-1}) for glyoxal. Species A_g and B_u.

	F_{11}	F_{22}	F_{33}	F_{44}	F_{55}	ν_2	ν_3	ν_4	ν_7	ν_8
1. calculation	10.9	4.5	4.8	0.6	0.9	1836	1458	956	1705	1392
2. »	10.9	4.5	4.8	0.6	0.8	1814	1412	942	1684	1330
Observed [9]						1745	1338	1060	1730	1312

b) Glyoxal. The point group of this molecule is C_{2h}. Only its in-plane vibrations, belonging to the species A_g and B_u, are treated.

The most interesting frequencies obtained are given in Table 3. Bending frequencies not involving hydrogen,and hydrogen stretching frequencies interact very little with carbonyl stretching and are therefore not listed. The same force constants were used for the antisymmetric vibrations as for the corresponding symmetric ones.

The diagonal force field results in a separation of 130 cm^{-1} between the symmetric and antisymmetric frequencies corresponding to carbonyl stretching, compared to only 15 cm^{-1} between the experimental values.[9] The inadequacy and crudeness of a diagonal force field are thus demonstrated again.

The two calculations listed show that the hydrogen bending force constant influences the carbonyl stretching frequency fairly strongly, if not quite as much as in the case of formaldehyde. Because the hydrogen bending constants of formaldehyde and glyoxal correspond to nonequivalent deformations, they cannot easily be transferred one into the other.

c) Acrolein. Acrolein is similar to glyoxal but has only C_s symmetry. A series of calculations on its in-plane vibrations gave results which were fairly analogous to the glyoxal results, including strong mixing of the C=C and C=O stretchings, in addition to the interdependence of C=O stretching and the various hydrogen bendings. However, even if the observed frequencies [9] were taken into account, it was not possible to relate the C=O stretching force constant of this molecule to values for either formaldehyde or glyoxal.

d) Acetaldehyde. This molecule has C_s symmetry and its ten A' vibrations are included in the calculations. The second to seventh diagonal force constants received the values (in md/Å) 4.5, 4.8, 4.8, 4.8, 0.6, and 0.9, respectively.

Table 4. Force fields (md/Å) and resulting frequencies (cm^{-1}) for acetaldehyde. Species *A'*.

	F_{11}	F_{88}	$F_{8,10}$	F_{99}	$F_{9,10}$	$F_{10,10}$	ν_4	ν_5	ν_6	ν_7
1. calculation	10.0	0.5	0	0.5	0	0.5	1756	1579	1420	1165
2. »	10.0	0.7	0	0.7	0	0.7	1720	1896	1475	1310
3. »	10.5	0.7	0	0.7	0	0.7	1743	1899	1479	1318
4. »	10.5	0.7	0.15	0.7	0.15	0.7	1782	1573	1473	1318
Observed [10]							1743	1441	1390	1352

The calculation method of Bratož and Besnaïnou resulted in a very small dependence of the carbonyl stretching frequency upon neighbouring methyl hydrogen bendings. The first two calculations of Table 4 demonstrate that a change in the bending constants of methyl hydrogens may have drastic effects involving also the carbonyl stretching frequency. There results a reversal of magnitude among two frequencies which is cancelled again by introducing two small interaction constants, as shown by the third and fourth calculations. The interaction constants bring the three calculated H bending frequencies closer together, as required by the observed values.[10]

The application of these few arbitrary force fields demonstrates that the methyl group of acetaldehyde is an additional obstacle preventing us from comparing the carbonyl force constants of different molecules.

e) Acetone. The same kind of calculations were performed and the methyl groups showed an interaction with carbonyl and a relation to observed frequencies [11] that were very similar to the acetaldehyde results. But even the carbonyl force constants of these two molecules could not be interrelated, because only acetaldehyde contains the aldehyde hydrogen that influences the actual force constant so strongly.

f) p- and o-Benzoquinone. Normal frequencies were calculated from diagonal force fields as for the other molecules. Observed frequencies were found only for *p*-benzoquinone.[12] This molecule showed a strong mixing of C=O and C=C stretching like acrolein, and a difference between calculated symmetric and antisymmetric C=O frequencies that was much too high, as in glyoxal. None of the calculated frequencies of *o*-benzoquinone showed a distinct carbonyl stretching character. We obtained only several frequencies composed of interacting C=O and C=C stretchings and H bending.

4. CONCLUDING REMARKS

Bratož and Besnaïnou [3] calculated carbonyl stretching force constants from observed frequencies by a method that had several advantages. The perturbation method applied allowed all other force constants, and even their effects on the carbonyl frequency, to be directly carried over from one molecule to another. Only one observed frequency for each molecule was needed, in addition to crude standard diagonal force constants, in order to perform the calculation. The results obtained were reasonable and the agreement with force constants predicted from MO theory was satisfactory.[2]

The present work was undertaken because we wanted an experimental test for a set of predicted force constants [1] as well as for the underlying semi-empirical MO calculation scheme.[6] It seemed favourable to refine the methods of Bratož and Besnaïnou somewhat by an exact solution of secular equations and by using all observed fundamental frequencies for most molecules.

Certain theoretical considerations indicated possible complications, however, and the results given demonstrate clearly the limitations imposed by these complications. The carbonyl stretching force constants of all the molecules treated in the present calculations, are evidently so inaccurately determined that realistic error limits are much larger than probable differences between any two of the constants. No means were obtained for establishing the relative order of magnitude of any two force constants, mainly because of the strong interactions of C=O stretching with C=C stretching and H bendings, including the bendings of the methyl hydrogens.

These results should be of some interest as it is clearly demonstrated how inaccessible single force constants are to evaluation from observed data, even in a case like carbonyl stretching with its distinct properties. Only the complete force fields can be adjusted to observed frequencies, and this process is not unique because the number of observable data is insufficient. Accurate force fields for most molecules, but the smallest, are therefore not obtainable at the present time.

Certain force constants, as for instance the hydrogen stretching constant, are known to be so independent of the remaining force field that they may be accurately determined. According to the present results, however, the carbonyl stretching force constants of organic molecules do not belong to this group.

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