

The Carbonyl Stretching Force Constant

I. A Molecular Orbital Study

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A simple formula for predicting carbonyl stretching force constants from semi-empirical MO calculations is suggested and applied to a series of molecules. In order to test the results properly more accurate force fields, based upon experiment, are required.

1. INTRODUCTION

The carbonyl stretching frequency is one of the most characteristic bond frequencies observed in the vibrational spectra of organic compounds. A few systematic attempts have been made to correlate spectral data related to the carbonyl group with results from semi-empirical molecular orbital calculations. Berthier *et al.*¹ several years ago reported a linear relationship between carbonyl stretching frequencies and Hückel bond orders for a series of molecules. Bratož and Besnainou^{2,3} introduced a more advanced treatment, attempting to separate the effects of vibrational coupling on the carbonyl frequency, from the effects of variation in the carbonyl stretching force constant. Carbonyl stretching force constants for seven molecules were estimated from a Pariser-Parr-Pople (PPP) SCF calculation,³ and compared to those derived from spectral data.² Forsén⁴ correlated carbonyl stretching frequencies observed in the vapour phase, with the bond orders resulting from a Hückel type calculation. He found a linear relationship for a series of 23 molecules, mostly halogen derivatives of formaldehyde, acetaldehyde, and acetone.

A new approach to the development of semi-empirical parameters for conjugated molecules in the PPP approximation has recently been introduced,⁵ and applied in a study of carbonyl compounds.⁶ The present work represents an attempt to combine this approach with the methods for deriving force constants from MO calculations, developed by Bratož and Besnainou.³ The resulting force constant estimates should be valuable as such, and furthermore they serve as a useful additional test on the applicability of the underlying parameter scheme.

2. THEORY

According to standard theory⁷ a force constant is defined by the following expression:

$$F_{ij} = \frac{\partial^2 V}{\partial S_i \partial S_j} \quad (1)$$

where V is the molecular potential function and where S_i and S_j are members of the complete set of linearly independent internal coordinates chosen in each particular case.

Bond distances and valence angles are well suited as internal coordinates. All of them usually cannot be incorporated in a linearly independent set. This often confuses the physical interpretation of certain force constants, because the partial derivative in (1) may have completely different meanings, depending on the choice of the remaining internal coordinates, not entering (1).

The carbonyl stretching force constant is a fortunate case from this point of view, however. A bond distance to an end atom is always easily varied in a manner not changing any valence angle or any other bond length. This particular force constant is thus invariant with respect to the choice of the remaining internal coordinates. According to (1) it is defined as follows:

$$F_{CO} = \frac{\partial^2 V}{\partial R_{CO}^2} \quad (2)$$

Now a formula for calculating carbonyl stretching force constants from semi-empirical PPP-MO calculations will be discussed. The treatment is closely connected to a derivation by Bratož and Besnainou.³ The modifications to their analysis and final formula introduced and discussed here, are partly due to the special semi-empirical parameter scheme underlying this work,^{5,6} and partly they are simplifications.

The derivation by Bratož and Besnainou starts from an expression in the atomic orbital basis for the part E of the molecular energy depending on interatomic distances. E is composed of a π -electron contribution E_π , and the energy of the underlying σ -core, E_σ , which is defined so as to include the mutual repulsions of atomic nuclei.

Bearing in mind that the atomic parameter W_μ is made dependent on the surroundings in our parameter scheme,^{5,6} we get the following expressions:

$$E = E_\sigma + E_\pi \quad (3)$$

$$E_\pi = \sum_\mu q_\mu W_\mu + \sum_{\mu < \nu} [2p_{\mu\nu} \beta_{\mu\nu} + (q_\mu q_\nu - q_\mu Z_\nu - q_\nu Z_\mu - \frac{1}{2} p_{\mu\nu}^2) \gamma_{\mu\nu}] \quad (4)$$

All symbols are chosen in accordance with standard notation.⁵

An expression for the carbonyl stretching force constant based on this formalism is obtained by replacing V in (2) by E as defined by (3) and (4). Making the same assumptions as Bratož and Besnainou, except for the properties of the parameter W_μ , and repeating their calculations, we arrive at the following formula:

$$\begin{aligned}
 F_{\text{CO}} = \frac{\partial^2 E}{\partial R_{\text{CO}}^2} = & [(1-p_{12})K_s + p_{12}K_d] + [\sum_{\mu} A_{1\mu} \gamma_{1\mu}''] \\
 & + [p_{12}' \{K_d(R_{12}-d) - K_s(R_{12}-s)\} + \sum_{\mu} A_{1\mu}' \gamma_{1\mu}'] \\
 & + [\sum_{\mu} \{(q_{\mu}-1)W_{\mu}'' + q_{\mu}' W_{\mu}'\}] \quad (5)
 \end{aligned}$$

where $A_{1\mu}$ is given by:

$$A_{1\mu} = (Z_1 - q_1)(Z_{\mu} - q_{\mu}) - \frac{1}{2}p_{1\mu}^2 + \frac{1}{2}\delta_{2\mu}p_{1\mu}$$

and where partial derivatives with respect to R_{CO} are indicated by dashes. The carbonyl oxygen and carbon are given the indices 1 and 2, respectively. R_{12} is the equilibrium length of the carbonyl bond (in contrast to R_{CO}). K_s and K_d are empirical parameters introduced as force constants for hypothetical pure single and double bonds, respectively. s and d are postulated equilibrium lengths of these bonds. $\delta_{2\mu}$ is a Kronecker delta.

The first three square brackets in (5) constitute the final formula of Bratož and Besnaïnou.³ The fourth square bracket is only a consequence of abandoning the assumption of a constant W_{μ} .

After this slight extension of the original formula it will now be claimed that only the first square bracket of (5) is of real importance in actual calculations. This means that F_{CO} is simply approximated as a linear function of the bond order. One strong reason for proposing this simplification is obvious when the two last columns of Table 1 are inspected. The force constants published by Bratož and Besnaïnou³ are quoted in column D. When only the linear bond order term of their formula is applied, however, the force constants of column E are obtained. The differences between the two sets are minimal, and by adjusting the empirical parameters K_s and K_d for each version of the formula, the differences can be made even smaller. It can safely be concluded that in this specific case the two sets of force constant estimates are completely equivalent for all practical purposes.

The present analysis was complicated by the fact that when the full expression (5) was used together with the semi-empirical parameter scheme applied in this work, certain ambiguities arose. However, some rough calculations indicated that the contributions of the three last square brackets in (5) to the force constants of this work would be approximately as small as demonstrated by columns D and E of Table 1.

It is thus tempting to suggest the following very simple interpolation formula for the prediction of carbonyl stretching force constants from PPP calculations.

$$F_{\text{CO}} = k_1 + k_2 p_{\text{CO}} \quad (6)$$

k_1 and k_2 are empirical constants to be determined from experiment. This treatment certainly could be extended to stretching force constants for other types of conjugated bonds as well.

Finally a prescription for determining k_1 and k_2 will be suggested. It is known from an investigation⁸ on several small molecules including H_2CO and D_2CO that the carbonyl stretching force constant of formaldehyde is close to

Table 1. Mobile bond orders for carbonyl bonds and various sets of carbonyl stretching force constants. See text for details.

Molecule	Bond order		Force constants				
	This work	This work	A	B	C	D	E
Formaldehyde	0.879	12.00	12.00	12.00	12.00	10.58	10.59
Acetaldehyde	0.831	11.69		12.05	11.84	10.42	10.44
Glyoxal	0.810	11.57	11.87		11.76	10.33	10.36
Acrolein	0.809	11.55	11.61				
Benzaldehyde	0.801	11.50	11.68				
Acetone	0.787	11.41			11.71	10.29	10.31
<i>o</i> -Benzoquinone	0.777	11.35	11.52		11.55	10.15	10.16
<i>p</i> -Benzoquinone	0.764	11.27	11.38		11.51	10.11	10.13

12 md/Å. Furthermore, it is a general experience that the force constants of various double bonds are roughly twice as large as those of the corresponding single bonds.⁷ This gives the following tentative working version of (6):

$$F_{\text{CO}} = \frac{12}{1 + p_{\text{CO}}^{\text{F}}} (1 + p_{\text{CO}}) \text{ md/Å} \quad (7)$$

were the superscript F stands for formaldehyde. To use this relation one needs carbonyl mobile bond orders for a set of molecules including formaldehyde. The carbonyl stretching force constant of any molecule in the set is then easily predicted.

3. RESULTS AND DISCUSSION

In Table 1 various sets of carbonyl stretching force constants are collected. The mobile bond orders shown in the second column were calculated and implicitly presented (as bond lengths) in a previous paper.⁶ The force constants resulting when relation (7) was applied to these bond orders, are given in the third column. The remaining columns of Table 1 are included for comparison. Those labelled A, B, and C, respectively, contain force constants obtained by applying (7) to the bond orders calculated by Berthier *et al.*,¹ Forsén,⁴ and Bratož and Besnainou.³ The two last columns finally show the force constants published by Bratož and Besnainou³ and those resulting from simplifying their formula, as has already been discussed in the section on theory.

The force constants of columns A and B are based on calculations of Hückel type, as mentioned in the introduction. The use of relation (7) in these cases has not been justified here. It is equivalent to neglecting the self-polarizability term in the well-known Coulson and Longuet-Higgins formula.⁹ The situation is somewhat analogous to the prediction of bond lengths by simple bond order relations. In the latter case a formula evaluated within the Hückel approximation¹⁰ was shown to be applicable also when an SCF procedure was used.¹¹

When the force constants of this work are compared with those based on the calculation of Bratož and Besnainou (columns C, D, E), it is seen that the

relative order of magnitude is the same in both sets, the main difference being a somewhat closer spacing within their series. The force constants from Hückel bond orders (column A) show a similar trend with only one reversal in order of magnitude. The calculations of Forsén predict a larger force constant for acetaldehyde than formaldehyde (column B), in contrast to the other results of Table 1.

The final test when predictions from MO calculations are discussed, should always be comparison with experiment. Bratož and Besnainou² derived some carbonyl stretching force constants from observed vibrational frequencies, using certain assumptions and approximations. They found a satisfactory agreement with the force constants predicted from PPP calculations.³ A similar derivation was planned as an essential part of the present work. However, as it is discussed in detail in a subsequent article,¹² it was not possible to obtain comparable carbonyl force constants for a series of molecules, even when all the observed fundamental frequencies for each molecule were taken into account.

The force constant estimates calculated in the present work should therefore only be taken as predictions. More accurate force fields, based upon experiment, are necessary in order to test the results properly.

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REFERENCES

1. Berthier, G., Pullman, B. and Pontis, J. *J. Chim. Phys.* **49** (1952) 367.
2. Bratož, S. and Besnainou, S. *J. Chim. Phys.* **56** (1959) 555.
3. Bratož, S. and Besnainou, S. *J. Chem. Phys.* **34** (1961) 1142.
4. Forsén, S. *Spectrochim. Acta* **18** (1962) 595.
5. Roos, B. and Skancke, P. N. *Acta Chem. Scand.* **21** (1967) 233.
6. Jensen, H. and Skancke, P. N. *Acta Chem. Scand.* **22** (1968) 2899.
7. Wilson, E. B., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw, New York 1955.
8. Müller, A., Krebs, B., Fadini, A., Glemser, O., Cyvin, S. J., Brunvoll, J., Cyvin, B. N., Elvebredd, I., Hagen, G. and Vizi, B. *Z. Naturforsch.* **23a** (1968) 1656.
9. Coulson, C. A. and Longuet-Higgins, H. C. *Proc. Roy. Soc. (London)* **A 193** (1948) 456.
10. Coulson, C. A. *Proc. Roy. Soc. (London)* **A 169** (1939) 413.
11. Skancke, P. N. *Acta Chem. Scand.* **18** (1964) 1671.
12. Jensen, H. H. and Cyvin, S. J. *Acta Chem. Scand.* **23** (1969) 3168.

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