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CHARACTERISTIC VIBRATIONAL FREQUENCIES OF CYCLIC KETONES*

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Abstract—The characteristic CO vibration frequency changes in small ring cyclic ketones are analyzed in terms of the kinetic energy effect of angle variation and the potential energy effects of hybridization and ring strain. A simple model is developed which accounts qualitatively for the effects; a more exact model is used for quantitative correlations. It is found that the changes in CO frequency are due almost entirely to the geometrical effect on the kinetic energy. Hybridization effects cancel out and play little role.

INTRODUCTION

AS ALMOST everyone knows, the characteristic IR absorption frequency of cyclic ketones at about 1700 cm^{-1} depends on the size of the carbocyclic ring. This phenomenon is used regularly as a diagnostic aid in structure determinations[1] since the absorption appears to be largely independent of factors such as alkyl substitution at the α carbon. It has been observed that a linear correlation exists between the frequency and the CCC angle at the CO group,[2,3] and in fact this correlation has been used to predict the angle in strained ketones with anomalous absorption maxima.[4,5]

Numerous attempts have been made to explain the effect. In general these have been qualitative arguments which appeal to intuition, although some quantitative work has been done.[2,6] A common explanation is associated with hybridization changes.[7] This is based largely on the relation of interorbital angle with the degree of hybridization, and the fact that the bond strength of hybrid orbitals increases with increasing *s* character (to a max at *sp*). Narrowing the CCC angle from 120° is said to cause an increase in *p* character in the ring bonds, and a corresponding increase in *s* character in, and thus a strengthening of, the CO bond.

It is clear, however, that an explanation based only on hybridization changes (in other words, force constant changes) cannot be completely correct since it is necessary to take into account the purely mechanical effect of the change in angle. The importance of this mechanical effect of the geometry can be seen from the work of Halford.[2] Making use of a 4-atom model, he made calculations which indicated that there is an appreciable dependence of the CO frequency on CCC angle due to mechanical effects alone, even if there are no changes in force constants (or hybridization) involved.

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The importance of the mechanical contribution was confirmed by Bratož and Besnaĩnou in a calculation making use of a perturbation technique,[6] and they were led to the conclusion that changes in the IR CO frequency of saturated cyclic ketones can be completely correlated with mechanical effect and that no change in the force constant or hybridization of the CO bond occurs.

Although both of the above mentioned studies examined the importance of the mechanical effect, neither looked at the role of changes in force constants or hybridization. Since such changes undoubtedly occur,[8] and since it is desirable to know to what extent the mechanical effect obviates the common interpretation in terms of hybridization, we have carried out more complete calculations taking into account the various parameters which might be involved. We first consider the mechanical effect and then the effect of changes in force constant or hybridization.

SIMPLIFIED MODEL

In considering the factors which influence the frequency at which the IR absorption occurs, it is convenient to consider separately those factors influencing the potential energy and those affecting the kinetic energy of a molecular vibration. The restoring forces involved (or the force constants) determine the potential energy. The kinetic energy is affected by the masses of the atoms and by the molecular geometry. The effect of atomic masses is obvious, but the geometrical dependence is somewhat more complicated. Therefore, to demonstate qualitatively the influence of CCC angle in the ketones discussed here, we shall first make use of a simplified model before making a more detailed calculation.

First consider the extreme cases of CCC angle equal to 180° (Fig. 1a) and 0° (Fig. 1b).

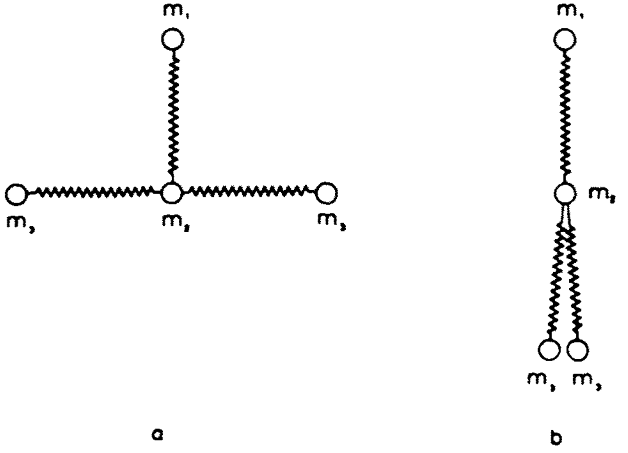

FIG. 1 Extreme cases of angle variation: (a) 180°, (b) 0°.

In the 180° case, the vibration of interest consists in large part of a bending of the CC bonds. Since bending vibrations are known to have small force constants, the vibration should have a low restoring force and a correspondingly low frequency. Alternatively, with an angle of 0°, the effect of the CC bonds is purely a stretch. Now, we expect a large force constant and high frequency.

For cases in between, there is an equally simple system. It is known, both from experiment and calculation (see later), that the normal vibration of interest is essentially independent of the mass of m_3;[9] let us consider the case in which m_3 is infinite. This corresponds to anchoring the simple model to a wall as shown in Fig. 2a. For the totally symmetric (A_1) vibration in this model we can simplify the system further as shown in Fig. 2b, where the value of the new force constant k'_{CC} is now $2k_{CC}$ Cos $(\theta/2)$.

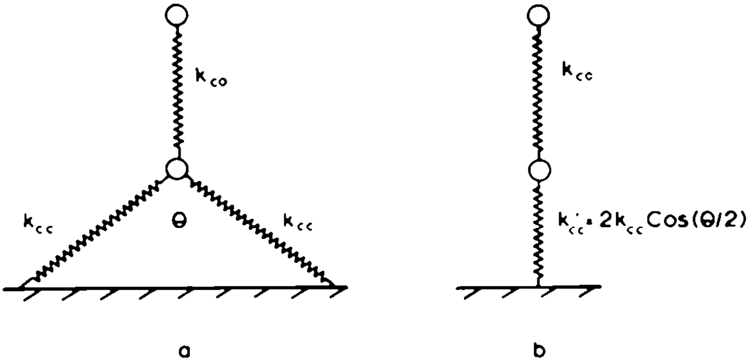

FIG. 2(a). Simple model anchored to wall, (b) Equivalent representation.

The bending force constant, being small, is neglected. The solutions to this problem are relatively simple ones,[10a] and the main feature is easily seen. In the vibration of interest, where bond CO is stretched, CC is compressed and conversely. Thus, the two bonds have an additive effect. Increasing either force constant raises the frequency, lowering either one decreases it. The reason for the effect of angle change now becomes qualitatively clear. If the force constants k_{CO} and k_{CC} are held constant, decreasing the angle increases $k'_{CC} = 2k_{CC}$ Cos $(\theta/2)$. Similarly the model suggests that the hybridization effects should tend to cancel. For although the CO bond is strengthened, the CC bonds are correspondingly weakened and the effective frequency is thus largely unchanged.

CALCULATIONS

In order to study quantitatively the details of the role of geometry and force constants we make use of a four-atom model. (Fig. 3) To justify our model, we must consider the nature of the characteristic CO vibration. To a good approximation, the vibrations of a molecule can be considered as those of a set of coupled harmonic oscillators in which all atoms participate in varying degrees. Wherever the force constants or atomic masses involved in a bond are sufficiently different from those of neighboring bonds, one of the normal modes of vibration will correspond roughly to motion in that bond alone. A well known example is the CH bond where the light mass of the H gives rise to a normal mode which is mostly CH stretching. In the case of a CO bond, the force constant is considerably larger than that involved in the neighboring CC bonds, and it might be expected that one normal mode of vibration would consist largely of stretching of the CO bond. Both theory and experiment verify this expectation, and, in fact, Halford[2] and Burkhard[9] have shown that the model of Fig. 3 provides an accurate description of the characteristic CO vibration.

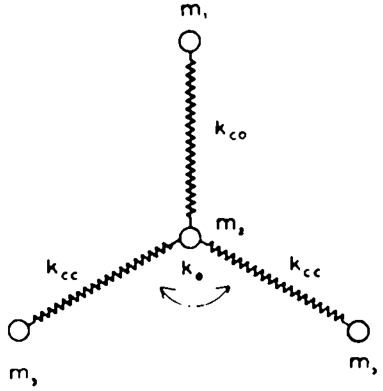

FIG. 3 Harmonic oscillator model for the carbonyl group.

In this model we neglect force constants not associated directly with bond stretching or bending (off diagonal **F** matrix elements set equal to zero). The frequencies of the totally symmetric (A_1) normal modes were calculated by using symmetry coordinates and appropriate masses in the **G** matrix, using reasonable force constants in the **F** matrix, and diagonalizing the unsymmetric product **FG** matrix.[10b] Use of a digital computer makes such an operation convenient and allows for an easy variation of parameters.

With an appropriate choice of parameters, this model accurately reproduces the characteristic frequency of aliphatic ketones. The values $k_{CO} = 10{\cdot}8 \times 10^5$ dynes/cm, $k_{CC} = 4{\cdot}5 \times 10^5$ dynes/cm, and $k_\theta = 1 \times 10^5$ dynes/cm were chosen to give $\nu = 1718$ cm^{-1} at 120°. These force constants are similar to those usually obtained in complete treatments of CO groups.[10c] In order to demonstrate the value of this model, calculated and observed[11] frequencies are listed in Table 1 for normal and isotopically substituted diiso-propyl ketone. The excellent agreement supports the validity of the model.

TABLE 1. CALCULATED AND OBSERVED FREQUENCIES OF ISOTOPICALLY SUBSTITUTED DIISO-PROPYL KETONE

	Calculated frequency	Experimental frequency*
Normal cpd.	1718 cm^{-1}	1712 cm^{-1}
Carbonyl C^{13}	1675	1675
Carbonyl O^{18}	1685	1681

* See Ref 11

With reasonable values of force constants, it had previously been shown that the frequency associated with the "carbonyl stretch" (1700 cm^{-1}) was relatively independent of the mass of m_3, provided $m_3 \geqslant 12$.[9] That is, there is little motion of these masses (atoms) in this vibration. We have confirmed this result. Similarly, this vibration is relatively insensitive to the bending force constant k_ϕ. Doubling this force constant causes only a small change (8 cm^{-1} or less) in the frequency irrespective of angle. It is convenient that these parameters have so little effect, since it makes subsequent evaluation of other parameters easier.

In Fig. 4 is shown the effect of variation of the angle θ on the calculated frequency. The solid line (calc) passes through the four calculated points for $\theta = 120°$, 108°, 90°, 60° (which are not shown). The equation is given by $\nu = -2{\cdot}4\theta + 2006\ cm^{-1}$.

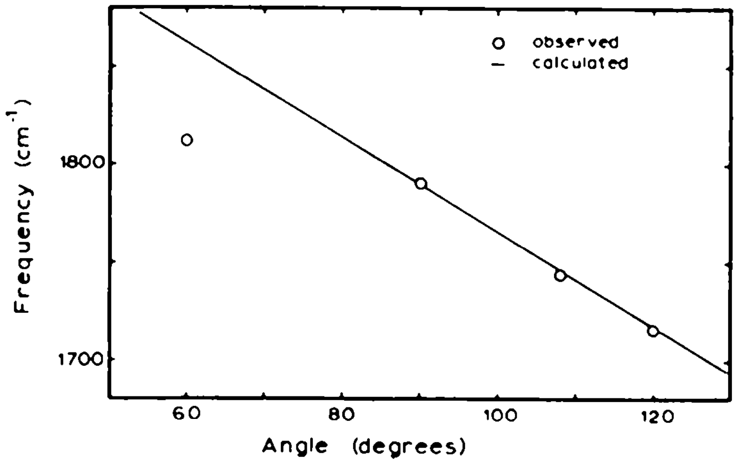

Fig. 4 Angular dependence of the characteristic carbonyl frequency.

This linear relationship of frequency and angle is similar to that obtained by Halford. It should be noted that this equation is based on calculations, and that use of it or any other similar equation for quantitative prediction of bond angles may not be justified in view of the undoubted effects of anharmonicity, vibration-rotation interactions, etc. It is not the purpose of this paper to emphasize the linear correlation implied by this equation, but rather to investigate the respective roles of hybridization and mechanical effects. However, it should be pointed out that the conclusion reached by Davis, Grosse, and Ohno,[12] that the *calculated* relation for ketones is non-linear in the range of 60°-120°, is based on an incorrect model. In their calculation, formaldehyde was used rather than the four-atom model used here. In formaldehyde, the very light mass of the hydrogens leads to considerable coupling between the CH motions and the CO stretch, and the vibrations behave in a qualitatively different manner than those in a molecule in which the hydrogens have been replaced by carbons.

The observed frequencies* for cyclohexanone, cyclopentanone, cyclobutanone, and cyclopropanone are also shown in Fig. 4. Table 2 shows the correspondence between calculated and observed[13, 14] frequencies for these compounds. Changing

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* Since published experimental values for the angles in cyclohexanone, cyclopentanone, cyclobutanone, and cyclopropanone are either unavailable or uncertain within the nominal values of 120°, 108°, 90°, and 60°, these values have been assumed in the calculations. The conclusions drawn from the calculations are independent of reasonable variations from the assumed values for the angles.

the value of k_{CO} changes the intercept of the line but not its slope. Thus the angular *variation* of frequency is essentially independent of the choice of k_{CO}.

TABLE 2. ANGULAR DEPENDENCE OF CARBONYL FREQUENCIES IN CYCLIC KETONES

Ketone (angle)[a]	Calculated Frequency[b] cm⁻1	Observed Frequency[c] cm⁻¹
cyclohexanone (120°)	1718	1716
Cyclopentanone (108°)	1746	1744[d]
Cyclobutanone (90°)	1790	1791
Cyclopropanone (60°)	1862	1813[e]

[a] See footnote on p. 9.
[b] k_{CO} = 10·8, k_{CC} = 4·5, k_ϕ = 1·0 (md/Å); m_1 = 16, m_2 = m_3 = 12.
[c] See Ref. 14.
[d] C. S. Foote, personal communication.
[e] See Ref. 13.

Although the experimentally observed variation of CO frequencies can be correlated with the effect of the angle change on the kinetic energy independent of force constants, there is undoubtedly some dependence of the force constant on angle. Thus we have also considered the effect of changing the force constants. If hybridization changes affect the strength of the CO bond, it is clear that the CC bond must also be affected, but in the opposite way. In order to estimate the effect of changes in force constant, the CO force constant was increased in increments of 0·1 × 10^5 dynes/cm and the CC force constant decreased by the same amount for each change in ring size. The results of this calculation are listed in Table 3, and show that, at least qualitatively, the hybridization effect tends to cancel out. This conclusion is independent of the increment chosen for the change in force constants.

TABLE 3. VARIATION OF FREQUENCY WITH FORCE CONSTANT

Compound (angle)	k_{CO}	k_{CC}	k_ϕ	Calc. freq.	Normal[a] calc.
Cyclohexanone (120°)	10·8	4·5	1·0	1718	1718
Cyclopentanone (108°)	10·9	4·4	1·0	1750	1746
Cyclobutanone (90°)	11·0	4·3	1·0	1795	1790
Cyclopropanone (60°)	11·1	4·2	1·0	1863	1862

[a] normal calculation using k_{CO} = 10·8, k_{CC} = 4·5, k_ϕ = 1·0

DISCUSSION

The assumption of small amplitudes for m_3 in the vibration of interest implicit in the 4-atom model is well borne out by the calculations. The small motion of m_3

is demonstated by the insensitivity of the calculated frequency to the mass of m_3. The CO frequencies calculated from the 4-atom model should, therefore, closely approximate those that would be obtained from a complete normal mode analysis. Furthermore, the detailed calculations confirm the conclusions derived from the simple model which assumes m_3 to be stationary. This can also be attributed to the small amplitude of m_3. Thus the simple model of Fig. 2 also serves as a useful way to demonstrate effects on the CO frequency. The small amplitude of m_3 is manifested experimentally in the observation that α substitution has little effect on CO frequencies.

The correlation of frequency with angle is remarkably good and accounts well for the observations for 4, 5, and 6 membered rings. It appears to be less valid for cyclopropanones. However, in order to understand the effects in very small rings, it is necessary to consider strain. The *empirical strain energy* of a molecule is the difference between the heat of formation observed and that calculated on the basis of bond properties of normal compounds. A somewhat more useful quantity in our case is the *vertical strain energy*.* This is the difference between the heat of formation observed and that calculated using corrected energies for bonds external to the ring (in this case CO and CH bonds) because the extended bonds are strengthened.[16] This strengthening is a consequence of the hybridization changes discussed previously. In general, the *vertical strain energy* will be greater than the *empirical strain energy*, and it provides a better measure of the weakening of CC bonds in the intact molecule. For example, the empirical strain energy of cyclopropane is about the same as that of cyclobutane,[17] whereas the vertical strain energy is greater. The origin of the added strain in cyclopropane is due, in part, to the inability of orthogonally hybridized atoms to combine in a 3-membered ring with optimum overlap -thus the usual picture of bent or "banana" bonds.[8] In conjunction with this CC bond weakening, the CC force constants will be substantially lower than normal. Since there is a lowering of the CC force constant without a completely compensating change in the CO force constant, one might reasonably expect the characteristic frequency of cyclopropanones to be lower than that calculated. Indeed, this is the case for cyclopropanone, the observed frequency falling below the calculated value by about 50 cm^{-1}. (Fig. 4) The reason for the absence of large effects of this type in strained systems such as bicyclic ketones may be that the "strain" is distributed over all of the bonds, and it is only those bonds adjacent to the CO group which are important.

In conclusion, we have demonstrated that the source of the variation of CO frequency in cyclic ketones is largely a kinetic energy effect and that the potential energy effects tend to cancel each other out. Correlation of the variation of CO frequency with hybridization changes has been found to be unjustified, and some possible effects of "strain" have been analyzed.

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