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VIBRATIONAL MODELS FOR TRANSITION STATES

METHANAL FOR METHYL CATION AND KETONES FOR THEIR CORRESPONDING CARBONIUM IONS[1]

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Abstract—The normal modes of vibration of methanal have been obtained. The frequencies of the three parallel vibrations have been computed as a function of the HCH angle using the best known force constants and bond distances. The vibrational solutions of methanal are then compared with the energetics of methyl cation, CH_3^+. While there is a functional dependence between the energy of CH_3^+ and the IR frequency of H_2CO with the same HCH angle, the relationship is not linear except over very small changes of the HCH angle.

Caution is recommended in accepting the current interpretations of the magnitude of anchimeric assistance using the Schleyer–Foote relationship between the carbonyl frequency and the energetics of carbonium ion reactions. In fact by a combination of quantum mechanical calculations and FG vibrational calculations, the slope of the Foote equation has been derived. The calculations show that deviations from the empirical Foote equation are to be expected and that the magnitude of the deviations are of the same order of magnitude as observed. However, these deviations occur in simple systems which have no chance of anchimeric assistance.

INTRODUCTION

IN THE previous paper[3] the computed properties of methyl cation using EHT theory were compared with two model systems: methanal and borane. The energy and charge distribution were calculated as a function of the bond lengths and bond angles. It was concluded that methanal is a stiffer model for methyl cation and borane is more plastic model even if the BH bond is shorted to a ^+CH length. Neither model system deforms in an isosteric manner[3] with methyl cation.

These EHT calculations were quite static in that the molecules were deformed to a certain geometry and then the properties computed. In the present paper, the dynamic vibrations along with normal modes of methanal and methyl cation are compared. It is an important comparison to make because several carbonium ion linear-free energy relationships using the carbonyl (or aldehyde) compounds have been suggested.[4-6]

RESULTS

The vibrations of H_2CO

This tetratomic system has been examined by numerous workers.[7] The tetratomic molecule has C_{2v} symmetry in the ground state and therefore has six nondegenerate vibrations (normal modes).

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[1] Paper II. Vibration Effects.

[2] [a] Alfred P. Sloan Fellow, 1962–1966; [b] National Education Defense Act Fellow; [c] Postdoctoral Research Associate.

[3] Paper I: R. E. Davis and A. Ohno, *Tetrahedron* **23**, 1015 (1967).

[4] C. S. Foote, *J. Amer. Chem. Soc.* **86**, 1583 (1964).

[5] P. von R. Schleyer, *J. Amer. Chem. Soc.* **86**, 1854 (1964).

[6] P. von R. Schleyer, *J. Amer. Chem. Soc.* **86**, 1856 (1964).

[7] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* pp. (*a*) 64–67, (*b*) 179–181, (*c*) 185, (*d*) 191–195, (*e*) 199–210, (*f*) 300–301, and (*g*) 474–490. van Nostrand, Princeton, New Jersey (1945); T. Shimanouchi and I. Suzuki, *J. Chem. Phys.* **42**, 296 (1965) and P. Cossee and J. H. Schachtschneider, *Ibid.* **44**, 97 (1966).

The solution to the H_2CO vibrational problem can be given in closed form.[7b,h,l] From the eigen vectors the atomic displacements can be obtained for each normal mode. The normal vibrations are present in Fig. 1. Five of the vibrations (ν_1 to ν_5) occur in the original plane of the molecule. The carbonyl–carbonyl stretching frequency is ν_2; it is a parallel vibration. The last vibration, ν_6, is the cut-of-plane carbonyl frequency. Using the best sets of force constants and the harmonic approximation, the observed gas phase infrared bands can be compared with the calculated bands. Since the molecules are so simple, the agreement of the experiment and theory is excellent. The results are reported in Table 1.

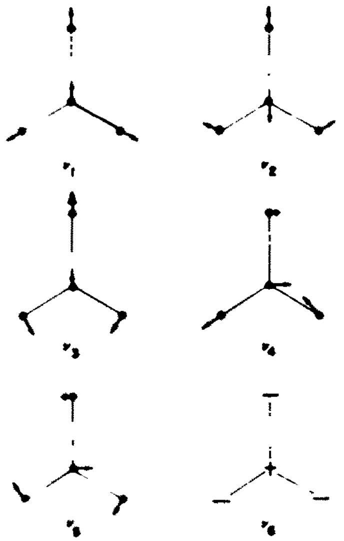

FIG. 1. Normal modes of vibration of methanal. Motions perpendicular to the plane of the molecule are indicated by + or – signs.

TABLE 1. THE VIBRATIONAL SPECTRUM OF METHANAL

Observed cm^{-1}	Symmetry	Calculated[a] cm^{-1}	Dev. cm^{-1}	Calculated[b]	Dev. cm^{-1}
2780	$a_1\ \nu_1$	2772	−8	2784	+4
1744	$a_1\ \nu_2$	1744	0	1746	+2
1503	$a_1\ \nu_3$	1504	+1	1499	−4
2874	$b_1\ \nu_4$	2882	+8	2868	−6
1280	$b_1\ \nu_5$	1284	+4	1263	−17
1167	$b_2\ \nu_6$	1167	0	1167[c]	0

[a] Valence Force Field Calculation calculated using the force constants reported by Cossee and Schachtschneider, Ref. 7*l*, in their Tables 10 and 13.

[b] Values calculated and reported in Ref. 7 by Shimanouchi and Suzuki.

[c] Recalculated in this study.

The values of ν_1, ν_2 and ν_3 (the carbon–hydrogen stretch, the carbon–oxygen stretch and the carbon–hydrogen bend, respectively) are related. All three of these parallel vibrations of a_1 symmetry are functions of the masses of the four atoms, the force constants, the $\cos^2\alpha$, and $\sin^2\alpha$ (where α is one half of the HCH angle;[7] see Table 1). All could be used to construct an equation like (2).

In Fig. 2 a plot has been constructed on the manner a carbonyl frequency, ν_2, varies as the HCH angle is varied. It is to be noted that the curve is definitely not linear. In fact the usual assumption that the frequency of the carbonyl can be used as

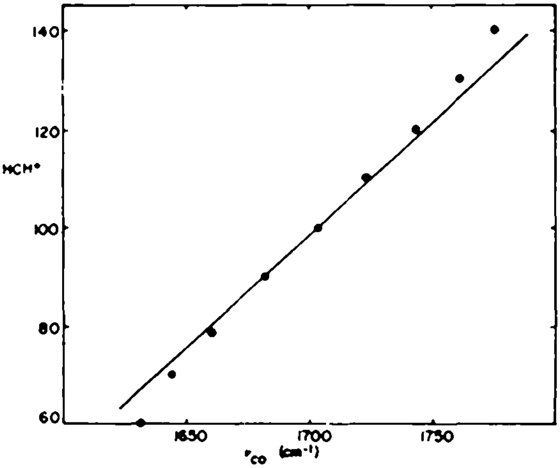

FIG. 2. Plot of the C=O stretching frequency in cm^{-1} as a function of the HCH angle in methanal. This is the second highest a_1 frequency in this system.*

quantitative measure of the HCH angle must be rejected;[8,9] unless, of course, the G and F matrices are known.

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* The H_2CO system has three a_1 bands. The highest band is called the CH band. If we were to plot v_1 versus the HCH angle a curve like Fig. 2 results. However, this curve which is also cubic, is of the opposite symmetry. The band in cm^{-1} decreases as the angle increases.

In the C_2CO system, the tetratomic model, used by Burkard and by Halford, the highest band is called the CO group frequency. The variation with CCC angle is given in Ref. 8. Since the bands are sensitive to the masses and both are a_1 bands, we can use the shift in band position in Fig. 3 and be theoretically correct. See Ref. 7*e*.

Note that since the mathematical form of the curve in Fig. 2 is a cubic (see Ref. 7*b*), we have not drawn a straight line but only the slope near the ground state of H_2CO.

A reviewer has commented on the use of Fig. 2 to predict the bond angle in cyclobutanone. This can not be done. In fact this represents a very good example that one must not take the force constants (F matrix) and the geometry and masses (G matrix) from one carbonyl system and use them without change in another system. See Ref. 8.

A well-known approximate relationship for the tetratomic C_2CO system was developed by J. O. Halford, *J. Chem. Phys.* **24**, 830 (1956). This approximation is known as the Halford equation and is:

$$\nu_{CO} = 1278 + 68k_1 - 2{\cdot}2\,\theta$$

where ν_{CO} is given in cm^{-1}; k_1, the carbonyl force constant, is given in mdynes/Å; and θ is the CCC angle in degrees. The Halford equation is an approximation as can be clearly seen if one allows the force constant to go to zero. The approximate equation predicts a finite "carbon frequency" even though the oxygen and the carbon atoms are no longer bonded to one another! Likewise, the limits as θ approaches zero or 180° are not those of the exact equations obtained by the vibrational solution.

Halford correctly noted the approximate nature of this equation. It has unfortunately been used by others as an exact equation[9] relating ν_{CO} to θ for numerous ketones.

We wish to acknowledge helpful correspondence with Professor Halford in the fall of 1965.

An example will be given showing the results of determination of the CCC angle at a carbonyl using the Halford equation. Cyclobutanone was suggested to have a bond angle of 82° by R. Zbinden and H. K. Hall, Jr., *J. Amer. Chem. Soc.* **82**, 1215 (1960) or 83·0° by P. von R. Schleyer and R. D. Nicholas, *Ibid.* **83**, 182 (1961) using the IR band. The recent microwave data show that the angle is 90° A. Bauder, T. Gäumann and F. Tank, ETH, Zurich; see the paper of K. Frei and H. H. Günthard, *J. Mol. Spectros.* **5**, 218 (1960).

The derivation of a vibrakinetic relationship

Foote[4] and Schleyer[5] have used a novel empirical relationship between the rate of reaction of the alcohol tosylate, RR'CHOTs, in acetic acid at 25° and the carbonyl frequency of RR'CO of the aldehyde or ketone. In particular

$$\text{RR'CHOTs} \xrightarrow[\substack{CH_3COOH \\ 25^\circ}]{k} \text{products as RR'CHOAc} \qquad (1)$$

Foote suggests

$$\log k/k_0 = -0{\cdot}132\,(\nu_{C=O} - 1720) \qquad (2)$$

where k_0 is the rate constant with cyclohexyl tosylate. In this equation $7{\cdot}57 \text{ cm}^{-1}$ is equivalent to a factor of 10 in rate. Schleyer suggests the angle strain term[5] has an equivalent form

$$\log k/k_0 = \tfrac{1}{8}(1715 - \nu_{CO}) \qquad (3)$$

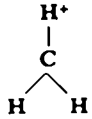
The important point is about 8 cm^{-1} increase in the carbonyl frequency decreases the rate by a factor of 10. Since a factor of 10 in rate is equal to about 1360 cal and 8 cm^{-1} is equal to 23 cal, the leverage of these vibakinetic relationships is about 59·6 to 1.

The data in Fig. 2 can be used as a deviation of the Eqs. (2) and (3). In Paper I the energy[1] of the methyl cation was obtained as a function of the HCH angle of the planar molecule. In Fig. 3 a plot has been presented relating the computed energy in ev of the CH_3^+ as a function of the HCH angle. However the HCH angle is then used to generate the position of the carbonyl frequency in CM^{-1}. The slope of the curve in the region of θ 116 to 108° is 7·5 cm^{-1} being equivalent to factor of 10 decrease in rate. Thus over small changes in the HCH angle one can use either Eq. (2) or (3) to accurately estimate the energetics of the corresponding carbonium ion. However, below this rather narrow range the slope rapidly increases. The data of Fig. 3 lead to the conclusion that for ketone with a small CCC angle at the carbonium the prediction of the rate will always be low. This is exactly what Foote and Schleyer observed. The data of Fig. 3 require that the slope of 7·57 cm^{-1}/10 in rate be for systems with *constant carbolny force constant.*

DISCUSSION

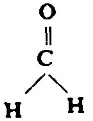
A serious question can be raised as to the usefulness of any one of the parallel vibrations as a model system for the energetics of a carbonium ion. First the similarities of the two systems must be noted.

(a) Both systems have valence C—H stretching force constants which are nearly the same.[10] This is reasonable and to be expected since in both systems the hydrogen atom is vibrating against an electron deficient carbon atom. The close agreement between the two values argues well for the reliability of our EHT calculation on methyl cation reported in Paper I.



4·47 mdynes/Å

C–H stretch



4·35 mdynes/Å

C–H stretch

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[10] In Paper I, the A_1' force constant (F_1') was computed using EHT theory[1]. Based on this method, the computed value is probably within 2% of the true value.

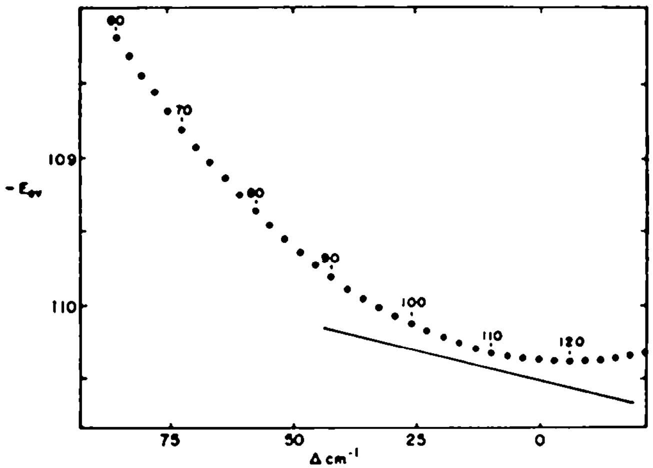
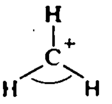
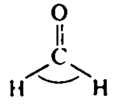


Fig. 3. Plot of the energy in ev of CH_3^+ as a function of the HCH angle in the cation versus the change in the carbonyl frequency in H_2CO for the same value of the HCH angle. The slope drawn is that of the vibrakinetic curve for angles of 108–116°. It has a value of 7·57 cm^{-1} per factor of ten in rate.*

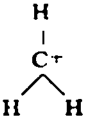
(b) Both systems have properties (charge density and energy, for example) that depends very heavily upon the rather similar[11] HCH angle, θ. The reasons listed, (a) and (b), argue well for the similarity. However, these two systems differ in several *extremely important aspects* which previously have been overlooked.[4–6]

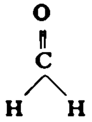




θ most stable θ'
120° form 116°

(c) The first great dissimilarity is the fact that the carbonium has a C—H bond stretch with a force constant of about 4·5 mdynes/Å while C=O force constant is


4·47 mdynes/Å


12·1 mdynes/Å

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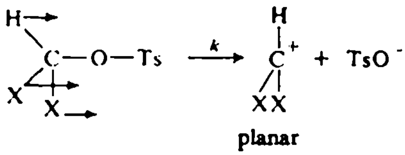
* The curve of Foote and Schleyer is obtained by plotting log k/k_0 versus ν_{CO}. We have duplicated these conditions using methane as our reference and computing the energy difference between the transition state CH_3^+ and its ground state methane as a function of the HCH angle and the energy difference between another geometry of CH_3^+ and its CH_4 ground state. In this curve about 6 cm^{-1} is equal to a factor of 10^{-1} in rate near 116°. However, this double difference curve shows greater curvature than even Fig. 3.

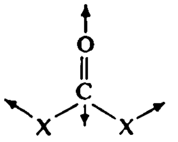
It should be noted that the data reported in Figs. 2 and 3 assumes that k_{CO}, the carbonyl force constant, is constant. Cyclobutanone has a smaller angle and a larger force constant than acetone. If we would add this also by assuming that k_{CO} increases slowly with geometry then the curvature of curve 2 and 3 are only increased as the carbonyl angle is decreased. Thus we believe our calculations represent a low estimate of the Foote–Schleyer slope. This is what we found; therefore, we feel that the deviations of Fig. 3 are also low!

[11] It is fortunate that the normal HCH angle in methanal is smaller than that of methyl cation. This means that the observed slope of the energy versus frequency curve is not zero. See Fig. 3.

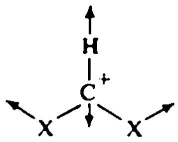
nearly 12 mdynes/Å for an aldehyde and 10 mdynes/Å for a ketone. This dissymmetry makes the carbonyl compound much more stiff to deform than the carbonium ion, a point which was also discussed in Paper I.

(d) More serious is the point that the carbonium ion is formed in a process in which a tetrahedral molecule is converted into a nearly planar ion. The carbonyl vibrational model chosen (as ν_{CO}) vibrates only *in this plane*. There is no bending out of the plane in this ν_3 vibration. In this aspect the ν_3 is a very poor model for the carbonium ion.





planar
2

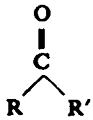


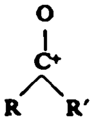
planar

The vibration of the planar carbonium ion is a normal mode that only increases the energy of the ion. It does not decompose the transition state and lead to products. Since the force constant is the second derivative of the potential energy, *increasing the force constant of the carbonyl would increase the energy of the carbonium ion.*

(e) One last small but bothersome point can be made. The activated complex of a carbonium ion is probably never completely planar. Besides the legate ion (leaving group)[12] would still be interacting with the developing C+. Thus it is another approximation to use a stiff-planar vibrational model for the activated complex.

These arguments and results obtained by sound theoretical considerations suggest that great caution ought to be used in any empirical relationship relating a parallel frequency of the model compound to a property (as the energy) of a corresponding carbonium ion. The same arguments are to be considered in more complex cases involving secondary carbonium ions and their model ketones:





In conclusion it is recommended that caution be observed in interpretation of results obtained from carbonium ion reactivities[4–6] and analogies drawn from vibrational data. In particular there are several properties of the carbonyl group that *over-estimate* the deformation properties of the carbonium ion. In the next paper of this series the vibrational behavior of cyclobutanone and cyclopropanone will be considered.

[12] R. E. Davis, *J. Amer. Chem. Soc.* **87**, 3010 (1965).

THEORETICAL

The vibrational calculations have been performed on an IBM 7094 using the method of Schachtschneidner and Synder.[13] Basically, the FG matrix has been modified to allow calculation of the frequencies from the G (geometric) matrix and the F (force field) matrix. The output includes the frequencies, and the eigen vectors.

The solution to the secular equation is by the Wilson G-matrix method using internal valence coordinates, R. The kinetic energy is given by

$$2T = \dot{R}'G^{-1}\dot{R}$$

and the potential energy by

$$2V = R'FR$$

Then

$$GFL = L\Lambda$$

where Λ is a diagonal matrix of the frequencies and L is the transform from normal co-ordinates, Q, to internal co-ordinates.

$$R = LQ$$

Using the Miyazawa method[14], the product GF, which is not symmetric, can be diagonalized by diagonalizing two symmetric matrices. Thus

$$GA = A\Gamma$$

Defining the transformation

$$W = A\Gamma^{1/2}$$

and operating on the F matrix

$$H = W'FW$$

H is symmetric since A is orthogonal and Γ is diagonal. H is then diagonalized:

$$HC = C\Lambda$$

and

$$W'FWC = C\Lambda$$

Then

$$GFWC = WC\Lambda$$

and

$$WW' = G$$

and

$$L = WC$$

The method is useful because (a) the L matrix is properly normalizing, (b) Jacobi's method can be used to diagonalize the symmetric matrices G and H, (c) the G matrix can be diagonalized by a separated program and T can be introduced since WW′ = G. Lastly redundant internal co-ordinates need not be removed before diagonalizing G.

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[13] J. H. Schachtschneider and R. G. Synder, *Spectrochim. Acta* **19**, 85 (1963).

[14] T. Miyazawa, *J. Chem. Phys.* **29**, 246 (1958).

This helps since vibrational problems with as many as 62 atoms have been solved with the Schactschneider–Snyder program.

Acknowledgements—The authors wish to thank the Petroleum Research Fund, the National Institutes of Health and the Fulbright Grant (for A. O.) for assistance. Dr. M. Wolfsberg supplied the copy of the program we have used in these calculations.

APPENDIX

The F matrix Used for H_2CO a_1 *and* b_1

Row 1	12·100000-	1·575700	1·5757000	−0·649200	0	0
Row 2	1·575700	4·351500	0	−0·314700	0	0
Row 3	1·575700	0	4·351500	−0·314700	0	0
Row 4	−0·649200	−0·314700	−0·314700	0·592800	0	0
Row 5	0	0	0	0	0·830500	0
Row 6	0	0	0	0	0	0·830500

(*a*) f_{11}. The CO constant.

Calculated ν_2 in the ground state was 1743·78 cm^{-1}, which is to be compared with 1744 observed.