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THE CARBONYL FREQUENCY OF ACETONE, ITS DEUTERATED AND O^{18} LABELLED SPECIES USING A FOUR ATOM MODEL, M_2CO[1]

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Abstract—Using normal coordinate analysis, the IR bands of the six fundamental skeletal modes of acetone have been computed using a four atom model. Refinement of the force constants allows prediction of all the normal modes of acetone to less than 4 cm^{-1} error in each band which approaches the experimental error of the IR measurements. However, the four atom model has faults which show up in such small structural variations as CD_3COCH_3 and CD_3COCD_3. Attempts to use the four atom model (the so-called Halford model) to correlate the position of IR bands are thus frustrated. Therefore, theoretical and speculative restraints are urged in the numerous attempts to relate ν_{CO} using a four atom model to such diverse problems as non-classical carbonium ions and the ν_{CO} band position of various cycloalkanones.

INTRODUCTION

IN PREVIOUS papers in this series, the theoretical and experimental consequences of using carbonyl stretching frequency as an energetic model and as a predictive (or *a posteriori*) tool for carbonium ion reactions have been discussed.[1, 3–5] Several conclusions were reached.

(1) No theoretical support could be given to the use of the Halford equation[6] (either directly or indirectly) or its implied linear relationship between $\underline{\nu}_{CO}$, the carbonyl stretching frequency in R_2CO, and the bond angle, RCR.

(2) Conclusion (1), when coupled to the well known fact that R_2CO compounds are stiffer and harder to deform than R_2CH^+ compounds, rules out the use of the $\underline{\nu}_{CO}$ to support non-classical carbonium ions.

In the present paper the use of the four atom model as suggested by Halford[6] has been extended to see if the four atom model could predict the skeletal frequencies of acetone, two of its deuterated derivatives (CD_3COCH_3 and CD_3COCD_3), and acetone $-O^{18}$.

THEORY

Several computer programs in FORTRAN IV have been used to set up and solve the GF vibrational secular equation.[7] CART, a program for evaluating the Cartesian coordinates of each atom (x_i, y_i, z_i), requires input information of bond distances and bond angles. Atomic masses are also entered. Basically the program computes the coordinates of each atom in a fixed coordinate system $\phi(x, y, z)$ from the bond angles and bond lengths. The first three atoms are used to define the coordinate system $\phi(x, y, z)$, whose origin is located on the first atom. The positive x-axis points in the direction of atom number two, and the triad 1-2-3 defines the x-y plane. For each additional atom a new coordinate system $\phi'(x', y', z')$, is used. The next atom is located by the spherical coordinates R, θ, and φ, in terms of its bond distances and bond angles. $\phi'(x', y', z')$ is located by giving the numbers of three previously defined atoms.

The program calculates the transformation, T, from $\phi'(x', y', z')$ to $\phi(x, y, z)$, determines the Cartesian coordinates x', y', and z' from the spherical coordinates r, θ, and φ, and transforms x', y', and z' to x, y, and z. The output consists of the x, y, z coordinates as well as the center of mass (and the principle coordinates) and the moment of inertia. The moment of inertia tensor is diagonalized by Corbato's SHARE subroutine.

GMAT, a program for computing the **G** matrix (or the vibrational inverse kinetic energy matrix), requires the input of the Cartesian coordinates,the masses of the atoms, and the numbers of the atoms defining a complete set of internal valence coordinates. An option is given for transformation to symmetry coordinates if this is desired. The vibrational problem, set up in the **GF** method, is expressed in internal valence coordinates (I.V.C.) satisfying the Eckart–Sayvetz conditions[8,9] to separate the vibrational problem for the translation and rotation of the molecule. The I.V.C. defined by Wilson[10] as modified by Decius[11] was used. The output of GMAT consists of punched cards containing the necessary matrix elements of the **X** matrix (Cartesian coordinates), the **B** matrix (matrix elements of the transformation $\mathbf{R} = \mathbf{B}\mathbf{x}$, from Cartesian coordinates, **x**, to internal coordinates, **R**), the **G** matrix (since **G** is symmetric only the diagonal and the above diagonal elements are punched), and the **U** matrix (elements of the transformation $\mathbf{S} = \mathbf{U}\mathbf{R}$ to symmetry coordinates, **S**).

These punched cards are then combined with the force constant elements (the **Z** matrix) and entered in to the next computer program that solves the complete vibrational problem. The output of this program consists of the calculated vibrational frequencies and the potential energy matrix. Options are available to print out the elements of the displacement vectors for each vibration.

RESULTS

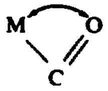
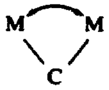
The structual parameters of acetone ($M_2C = O$) were taken from the microwave data of Swalen and Costain:[12] $r_{C=O} = 1{\cdot}215$ Å, $r_{C-M} = 1{\cdot}515$ Å, $\angle$ MCM $= 116° 7'$. Masses were $0 = 16{\cdot}000$; $C = 12{\cdot}011$, and $M = 15{\cdot}035$ since a four atom model is being used. The mass of M was increased for the d_3 and d_6 compounds. In Tables 1 and 2 the valence force constants, the interactions constants, and definition of the internal coordinates are given. The values of the force constants used in Problem No. 6 (Table 3) are listed in Tables 1 and 2.

The force constans were obtained from Beckmann[13] for Problem No. 1. The best constants of Cossee and Schachtschneider[14] were used for the calculations of Problem No. 2. The results are given in Table 4. The experimental values are those reported by Dellepiane and Overend.[15] The value of $\Delta\nu$ is the *absolute value* of the difference of the calculated value and the experimental value. The value of $\Delta\nu$ is the average deviation of estimate of all six fundamental modes of a four atom system, M_2CO.

It is seen that the average deviation from the observed frequencies of acetone is 19 wave numbers for Problem #1 and 28 wave numbers for Problem #2. Since the force constants of Problem #1 calculated the best frequencies it was decided to refine these constants to see if a still better fit could be obtained. In Table 3 the values of the force constants used in Problem #3–6 are also given. The results of these calculations are found in Table 4.

From Table 4 it can be seen that as a better fit for the observed frequencies of acetone is obtained, the average deviation between calculated and observed frequencies for

TABLE 1. VALENCE FORCE CONSTANTS ASSIGNED TO INTERNAL COORDINATES FOR THE SKELETAL VIBRATIONS OF ACETONE USING A FOUR ATOM MODEL

Coord. No.	Description	Code[a]	Force constant	
			No.	Value[b]
1	C=O	1	1	10·50
2	C—M	1	4	4·24
3	C—M	1	4	4·24
4		2	6	0·892
5		2	6	0·892
6		2	7	0·595
7	Carbonyl Out-of-Plane Bend	3	8	0·366

[a] 1 ≡ stretch (weighing factor = 0, 0); 2 ≡ bend (weighing factor = 1, 1); 3 ≡ out-of-plane bend (weighing factor = 1, 1).

[b] Stretching constants in units of millidynes per angstrom. Bending constants in units of millidynes angstrom per square radian.

Values of Problem 6, see Table 3.

TABLE 2. INTERACTION FORCE CONSTANTS USED IN THE SKELETAL VIBRATIONS OF ACETONE USING A FOUR ATOM MODEL

Coord. Nos.	Description	Force constant	
		No.	Value[a]
1–2	C=O and C—M interaction	2	−0·176
1–3	C=O and C—M interaction	2	−0·176
1–6	C=O and 	3	−0·219
2–3	C—M and C—M (C in common)	5	1·478

[a] Stretch-bend interaction constants in units of millidynes per radian. Values of Problem 6, see Table 3.

the deuterium substituted compounds gets larger. This indicates that the force field used is not as good an approximation as would be desired. For example, the force constants of Problem 6 of Table 4 (and listed in Tables 1–3) give an average deviation, $\overline{\Delta\nu}$, of only 4 cm^{-1}, an extremely small number for acetone. However, CH_3COCD_3, (or MCOM′) has an average deviation of 25 cm^{-1} with large errors of prediction in each normal mode except the C=O stretching mode. In the fully deuterated compounds the $\overline{\Delta\nu}$ increases to 44 cm^{-1}.

TABLE 3. SUMMARY OF FORCE CONSTANTS[a] USED IN THE SKELETAL VIBRATIONS OF ACETONE, PROBLEMS 1–6

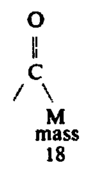
Force Constants[a]

Problem No.	F_{11}	$F_{12} = F_{13}$	F_{16}	$F_{22} = F_{33}$	F_{23}	$F_{44} = F_{55}$	F_{66}	F_{77}
1	10·50	0	0	4·24	0	0·892	0·595	0·353
2	9·723	0	0	4·077	0	1·001	1·649	0·217
3	10·50	−0·176	0	4·24	0	0·892	0·595	0·353
4	10·50	−0·176	0	4·24	0·478	0·892	0·595	0·353
5	10·50	−0·176	−0·269	4·24	0·478	0·892	0·595	0·363
6	10·50	−0·176	−0·219	4·24	0·478	0·892	0·595	0·366

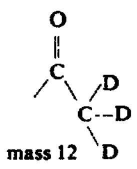
[a] Stretching constants in units of millidynes per angstron. Bending constants in units of millidynes · angstrom per square radian. Stretch-bend interaction constants in units of millidynes per radian.

The reader should also note that the C—C stretching band (1216 cm^{-1} experimental in acetone) is increased to 1224 cm^{-1} (experimental) in CH_3COCD_3 and to 1242 cm^{-1} (experimental) in CD_3COCD_3. However, the four atom approximation puts all of the mass of each CH_3 or CD_3 group into a unified atom, MD. or M′.

Thus, one gets the calculationally expected result that as M increases in mass, the M—C stretching frequency would drop (see Table 5). Problem 6 predicts a shift of −23 cm^{-1} upon full deuteration, in the opposite direction of the experimental observed effect of +26 cm^{-1}. Thus to obtain the proper magnitude and direction of the shift, one must go to a full atom treatment



incorrect shift
of νC—C *vs* mass



correct shift
of νC—C

using force fields of each atom in the acetone molecule (calculational results on CH_3COCH_3 and CD_3COCD_3 using the full force fields are unpublished data from these labs).

Thus we cannot over emphasise the fact that four atom models should not be used

TABLE 4. CALCULATED AND OBSERVED SKELETAL FREQUENCIES OF ACETONE AND THE ISOTROPICALLY SUBSTITUTED ACETONES, PROBLEMS #1–6

Compound	Observed[a] Frequencies cm^{-1}	Calculated frequencies																	
		Prob. 1	$\Delta\nu$	$\overline{\Delta\nu}$	Prob. 2	$\Delta\nu$	$\overline{\Delta\nu}$	Prob. 3	$\Delta\nu$	$\overline{\Delta\nu}$	Prob. 4	$\Delta\nu$	$\overline{\Delta\nu}$	Prob. 5	$\Delta\nu$	$\overline{\Delta\nu}$	Prob. 6	$\Delta\nu$	$\overline{\Delta\nu}$
Acetone	1731	1723	8		1709	22		1743	12		1753	22		1727	4		1732	1	
	1216	1271	55		1267	51		1271	55		1212	4		1212	4		1212	4	
Acetone	786	761	25	19	756	30	28	751	35	22	785	1	8	789	3	5	788	2	4
	484	496	12		517	33		496	12		489	5		490	6		490	6	
	385	393	8		408	23		393	8		394	9		397	12		397	12	
	530	520	10		541	11		520	10		520	10		528	2		530	0	
		1693			1683			1712			1724			1697			1702		
		1270			1266			1270			1211			1211			1211		
Acetone-^{18}O	[b]	750			742			740			774			776			776		
		484			536			484			478			478			478		
		389			504			390			390			394			393		
		517			405			517			517			525			527		
	1734	1722	12		1708	26		1741	7		1751	17		1725	9		1730	4	
	1224	1258	34		1256	32		1258	34		1201	23		1201	23		1201	23	
ααα-Acetone-d_3	740	738	2	23	736	4	33	728	12	24	762	22	24	765	25	25	765	25	25
	438	484	46		503	65		484	46		477	39		477	39		477	39	
	352	380	28		406	54		381	29		381	29		384	32		384	32	
	502	518	16		521	19		518	16		518	16		525	23		527	25	
	1732	1721	11		1706	26		1721	7		1750	18		1723	9		1728	4	
	1252	1245	3		1243	1		1245	3		1189	53		1189	53		1189	53	
Acetone-d_6	696	714	18	31	716	20	40	705	9	29	738	42	43	741	45	44	741	45	44
	405	473	68		492	87		473	68		466	61		466	61		466	61	
	321	367	46		404	83		367	46		368	47		371	50		370	49	
	475	515	40		500	25		515	40		515	40		522	47		525	50	

[a] Experimental values. See Ref. 15.

[b] Gas phase spectrum is under study in these laboratories.

TABLE 5. EFFECTS OF MASS UPON THE C—C STRETCHING FREQUENCY

			Results of the four atom model calculations			
	Experimental cm^{-1}[a]	$\Delta\nu$[b]	Model 1	$\Delta\nu$[c]	Model 6	$\Delta\nu$[e]
CH_3COCH_3	1216	0	1271	0	1212	0
CD_3COCH_3	1224	+ 8	1258	−13	1201	−11
CD_3COCD_3	1242	+26	1245	−26[d]	1189	−23

[a] See Table 4.

[b] Computed $\Delta\nu$ from CH_3COCH_3; 1224 − 1216 = +8 for CD_3COCH_3.

[c] Computed shift from MCOM to M′COM to M′COM′ using Model 1.

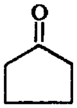
[d] For example, 1245 − 1271 = −26 cm^{-1}.

[e] Shift computed using Model 6.

to relate the observed frequencies to the calculated results. For example, recently[16] the cyclic ketones

1

2



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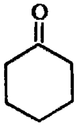

4

have been treated using a tetra atomic model using only diagonal force constants and computing the change in $\Delta\nu_{CO}$ as the  $C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C$ angle is varied. While reasonable values were computed for the ν_{CO} of 2, 3 and 4, the error of prediction of ν_{CO} of 1 was about 50 cm^{-1}. The model used (see Table 2 of ref 16) had constant force constants (k_{CO} = 10·8 mdynes/Å) for all ketones 1–4; that is, an assumption which is known to be false since the carbonyl force constants varies by about 0·5 mdynes/Å in compounds 1 to 4.

O^{18} *Acetone*

It is of interest to note that a shift of 29 cm^{-1} (gas phase) for the ν_{CO} frequency is predicted by these calculations (Problem 6, Table 4) for $(CH_3)_2CO^{18}$. This value can be compared with the experimental values of 33 cm^{-1} in acetonitrile solution[17] and 30 cm^{-1} in water.[18] Currently O^{18}-enriched acetone is under study in the gas phase. In particular the use of the isotopic shifts is being made to settle some fundamental problems of band assignments in acetone and other ketones.

These calculations on the O^{18} derivative can be used as an aid to the experimental problem of determining the out-of-plane carbonyl bending frequency by oxygen-18 isotopic substitution. These calculations predict very small oxygen-18 shifts for the bands below 600 cm^{-1}. The 530 cm^{-1} band (which is the out-of-plane carbonyl bend by this calculation) shifts only 3 wave numbers to 527 cm^{-1} in acetone-^{18}O. The calculated 397 cm^{-1} band of acetone shifts to 393 cm^{-1} in acetone-^{18}O, a shift of 4 wave numbers. The 490 cm^{-1}, which is 77% carbonyl in-plane bend (see Table 6) is lowered 12 wave numbers to 478 cm^{-1} in acetone-^{18}O.

In Table 6 the potential energy matrix is given for Problem 6. The numbers change by very little by small changes in the force constants (Table 4). The symmetry of each fundamental mode is clearly seen by the O elements in the matrix. For example, only F_{77} determines the position of ν_6, the out-of-plane bend.

TABLE 6. NORMALIZED POTENTIAL ENERGY DISTRIBUTION OF ACETONE, PROBLEM #6

ν	F_{11}	$F_{12} = F_{13}$	F_{16}	$F_{22} = F_{23}$	F_{23}	$F_{44} = F_{55}$	F_{66}	F_{77}
1732	0·8315*	0·0230	0·0251	0·1146	0·0129	0·0185	0·0246	0
1212	0	0	0	0·8709	−0·0982	0·2273	0	0
788	0·1688	−0·0266	0·0068	0·7506	0·0846	0·0067	0·0090	0
490	0	0	0	0·2562	−0·0289	0·7727	0	0
397	0·0054	0·0010	0·0094	0·0347	0·0039	0·4051	0·5405	0
530	0	0	0	0	0	0	0	1·0000

* The underlines values show the largest contribution of purity to each normal mode.

Using Table 6, the calculated band at 1732 cm^{-1} is made up of 83% carbonyl stretch and 11% of C—C stretch. The asymmetric C—C stretching band at the calculated value of 1212 cm^{-1} is made up of 87% of the C—C stretch. Likewise, the symmetric C—C stretch at the calculated value of 788 cm^{-1} is made up of 75% C—C stretch. The calculated band at 490 cm^{-1} turns out to be made up of 77% of the carbonyl in-plane bending motion. The band at 397 cm^{-1} is due to the coupled vibration of both the carbonyl in-plane bend and the carbonyl angle bend. It is made up of about 54% of the carbonyl in-plane bending vibration. These calculations show that the carbonyl out-of-plane bend is the band at 530 cm^{-1} which depends only upon the F_{77} force constant. With the exception of that normal mode, none of the vibrational modes are "pure" motions. While these ideas are not new, it is felt that the practising organic chemist sometimes loses sight of some theoretical insights. Had these facts been well known and appreciated, one doubts if anyone would have misused the original Halford equation as a structural tool to "measure" C—C—C angles in ketones.

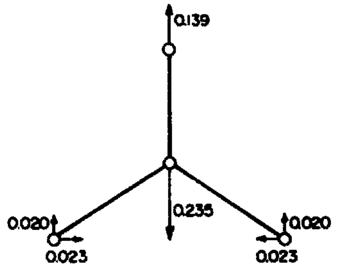

FIG. 1 Motion of atoms displaced by the normal mode with a frequency of 1732 cm^{-1}.

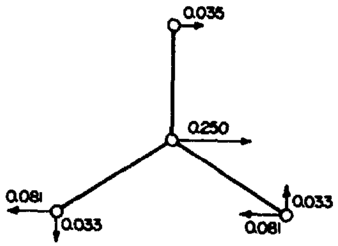

FIG. 2 Motion of atoms displaced by the normal mode with a frequency of 1212 cm⁻¹.

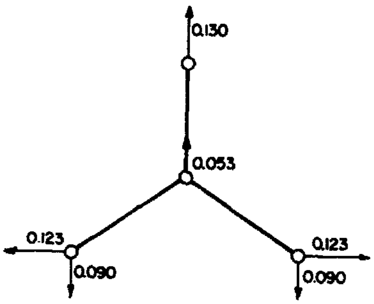

FIG. 3 Motion of atoms displaced by the normal mode with a frequency of 788 cm⁻¹.

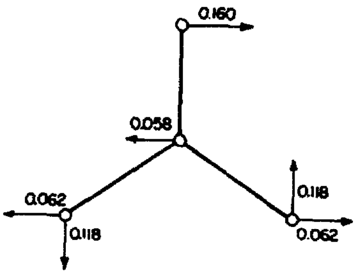

FIG. 4 Motion of atoms displaced by the normal mode with a frequency of 490 cm⁻¹.

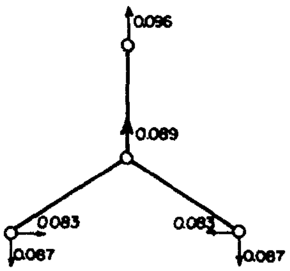

FIG. 5 Motion of the atoms displaced by the normal mode with a frequency of 397 cm⁻¹.

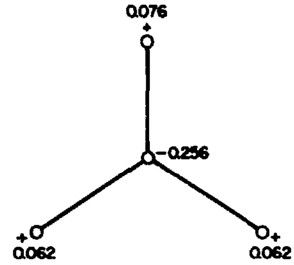

FIG. 6 Motion of atoms displaced by the normal mode with a frequency of 530 cm^{-1}.

In Figs 1–6 the displacements from the equilibrium position of the atoms in the four atom model are given. The elements of the displacement vectors, whose origins are at the given atom, are shown. These vectors give the direction of the straight-line motions (in the x, y, z directions) of the n atoms vibrating in normal mode i and the lengths show the relative amplitudes for each atom. These relative displacements clearly show that in the ν_{CO} band not only the oxygen and carbon move in the carbonyl group, but that the other atoms move a bit to maintain a constant center of mass of the molecule. Since ν_{CO} has a 11% part of the C—C stretch (see Table 6) and a 2% contribution of the C—C—C bend (force constant F_{66}), one can "see" why the ν_{CO} does depend upon the C—C—C angle but in a rather complicated manner.

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