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Normal coordinate analysis and spectral band assignments of the normal vibrations of deutrated acetate anion

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* A. Uzairu, G.F.S. Harrison and A. Abdulhamid
Department of Chemistry, Ahmadu Bello University, Zaria-Nigeria

ABSTRACT

Results of the normal coordinate analysis on the $CD_3CO_2^-$ ion suggest a revision of previous assignments of some of its infrared absorption bands. Thus, the empirical suggestion of accidental degeneracy amongst CD_3 stretching modes is not supported by our calculations and, accordingly, the bands at 2183 and 2167 cm^{-1} are due to $\upsilon_s(CD_3)$ and $\upsilon_{as}(CD_3)$, respectively, and not $\upsilon_{as}(COO)$ + $\delta(COO)$ and $2\delta_s'(CD_3)$ combination and overtone bands. Also, the bands at 880 and 928 cm^{-1} formerly assigned to pure C-C stretching and CD_3 rocking modes are now $r_s(CD_3)$ coupled with $\delta_s(CD_3)$ and $\delta_s'(CD_3)$, and υ(C-C) coupled with $\upsilon_s(COO)$ and $\delta_s(CD_3)$ modes, respectively.

* Author for correspondence

INTRODUCTION

The infrared spectrum of $CD_3CO_2^-$ ion has been studied in the past, particularly by Jones and McLaren [1]. These two authors noted the similarity of the $CD_3CO_2^-$ to the CD_3NO_2 molecule, for which normal coordinates analysis was done [2]. By comparing the infrared spectra of the two compounds, Jones and McLaren made empirical assignments of the frequencies of the former.

However, it is well known that such an empirical approach encounters serious difficulties in some cases. For instance, Jones and McLaren themselves acknowledged the confusion and arbitrariness involved in (i) choosing between 525 and 609 cm^{-1} for COO deformation frequency, and (ii) assigning υ(C-C) and three CD_3 rocking frequencies in the 800-950 cm^{-1} region. In addition, their study did not assign CD_3COO torsional mode about the C-C bond. Also, the band at 2254 cm^{-1}, which was attributed to two accidentally degenerate CD_3 stretching vibrations, has attracted our attention for two reasons. Firstly, even normal coordinate calculations carried out later by Nakamura on this ion [3], employing Urey-Bradly (UB) force field, came to the same conclusion. The second reason is that CD_3 group in higher deuterated RCO_2^- ions [4] and $CH_2(OH)COOCD_3$ [5] were found to have three distinct stretching frequencies and not just two.

As mentioned above, Nakamura's study, which is the only normal coordinate analysis made on the $CD_3CO_2^-$ ion so far, was based on the UB force field. But the inadequacy of the UB field is very well known; interactions between bending modes are absent in it and apparently, a few of these are important. In acetone and dideuteroacetone, for example, it was not possible to obtain agreement at the same time for the frequencies belonging to the CH_3 rocking and to the symmetrical CH_3 deformation without the introduction of interaction between bending modes [6]. The necessity of these modifications greatly reduces the attractiveness of the UB approximation since the choice of the extra interaction constants is of partly arbitrary nature. Thus, the question of whether a UB force field is a suitable approximation to describe the normal vibrations of a molecule such as $CD_3CO_2^-$ ion, which has more bending coordinates than any other type, is obvious.

In view of the reasons stated above as well as the conflict in the assignment of CD_3 stretching frequencies in $CD_3CO_2^-$ ion with higher deuterated RCO_2^- ions and $CH_2(OH)COOCD_3$, and, also, to assign the CD_3COO torsional mode for the first time, it was considered important to revisit the calculations of the normal vibrations of the $CD_3CO_2^-$ ion, this time, using a generalized valence force field. This potential field allows interaction between any two types of coordinates in the harmonic approximation and is by far the most powerful of the force fields [7].

METHOD OF CALCULATION

The $CD_3CO_2^-$ ion, shown in Fig. 1, has a $\mathbf{C_S}$ symmetry. The fifteen normal vibrations of this ion are

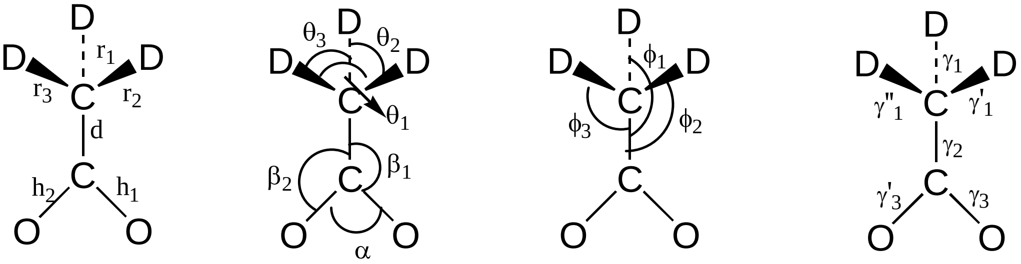

Figure 1: The elementary internal coordinates of $CD_3CO_2^-$ ion

separable into $9A^{/}$ $+2A^{//}$ in-plane and $4A^{/}$ out-of-plane vibrations. The out-of-plane vibrations are the deformation motions that are anti-symmetric with respect to the plane of the ion, $\boldsymbol{\sigma_h}$. Both the in-plane and out-of-plane vibrations are calculated. The independent internal coordinates are shown in Table 1 and the elements of the **G** matrices for the various classes of vibrations of the ion were calculated according to a standard method in the literature [8]. At present, most authors use the transferable valence force field. In order to facilitate a comparison with force fields by other authors, we have made use of this type of valence force field. The **F** matrix was thus constructed following the conventions of Hollenstein and co-workers [5, 9], which are widespread in the literature on the subject. The application of those criteria left 30 force constants for the $CD_3CO_2^-$ ion. Initial force constants for the CD_3-C fragment of the ion were taken from the force fields of methyl acetate [5] and acetone [6], which are transferable valence force fields. The matrix secular equations, $|\,\mathbf{GF} - E\Lambda\,| = 0$, were then solved for each species of both the in-plane and out-of-plane vibrations of the $CD_3CO_2^-$ ion.

The calculations were made with the aid of the $CD_3CO_2^-$ dimensions taken from ref. 1. After several iterations, a satisfactory set of force constants, listed in Table 2, was obtained. In Table 3, the frequencies calculated from this set of force constants are compared with the values observed for the ion [1]. Agreement between the calculated and observed values is quite satisfactory for both in-plane and out-of-plane vibrations. In order to make theoretical band assignments and to determine the mixing ratio of various modes in each band, the potential energy distribution (PED) in each normal vibration [10] was calculated with respect to each independent internal coordinate.

RESULTS AND DISCUSSION

On the basis of the results of the potential energy distribution calculated, all the normal vibrations of the $CD_3CO_2^-$ ion were theoretically assigned. The bands at 2254 (υ_2), 2183 (υ_1) and 2167 (υ_9) cm^{-1} represent the frequencies of the pure CD_3 stretching modes; the bands at 2183 and 2167 cm^- are not, respectively, $\upsilon_{as}(COO)$ + $\delta(COO)$ and $2\delta_s'(CD_3)$ combination bands as were assigned by previous investigators. Also, the results reveal no accidental degeneracy amongst CD_3 stretching vibrations. The bands at 1563 (υ_{10}) and 1406 (υ_4) cm^{-1} are, respectively, υ_{as} (COO) and $\upsilon_s(COO)$ modes ; they are pure vibrations (99% up). The splitting between the frequencies of the $\upsilon_{as}(COO)$ and $\upsilon_s(COO)$ modes is rather large due to strong interaction between the two C-O bonds.

The following bands at 1081(υ_8), 1045 (υ_{13}) and 1030 (υ_7) cm^{-1} are $\delta_s'(CD_3)$ coupled with $r_s(CD_3)$, $\upsilon_s'(CD_3)$ and $\delta_s(CD_3)$, $\delta_{as}(CD_3)$ coupled with $r_{as}(CD_3)$ and $\upsilon_{as}(CD_3)$, and $\delta_s(CD_3)$ coupled with $\upsilon_s(C\text{-}C)$ modes, respectively. Thus, the CD_3 deformation vibrations are not pure vibrations, as the results indicate, and, since $\mathbf{A'}(C_s)$ transforms as $\mathbf{A_1}$ + $\mathbf{B_2}$ ($\mathbf{C_{2v}}$), then it is in order that the 1030 cm^{-1} band, formerly assigned as belonging to the $\mathbf{B_2}$ class [1], now be of $\mathbf{A'}$ representation.

The bands at 880(υ_6), 828(υ_{12}) and 928(υ_3) cm^{-1} are $r_s(CD_3)$ coupled with $\delta_s(CD_3)$ and $\delta_s'(CD_3)$, $r_{as}(CD_3)$ coupled with $\delta_{as}(CD_3)$ and υ(C-C) coupled with $\upsilon_s(COO)$ and $\delta_s(CD_3)$ modes, respectively. The 880 and 928 cm^{-1} bands are of specially interest since these were formerly assigned [1] as pure C-C stretching and CD_3 rocking modes, respectively. Also, the bands at 525(υ_{14}) and 411(υ_{11}) cm^{-1} are due to $r_s(COO)$ and $r_{as}(COO)$ pure vibrations according to the results of the calculations. On the other hand, the band at 609(υ_5) cm^{-1} was assigned to $\delta(COO)$ coupled with $\upsilon_s(COO)$ and $\delta_s(CD_3)$ modes. However, band for CD_3COO torsion is rather

Table 1: Definition of internal coordinates of the $CD_3CO_2^-$ ion.

Definition	Vibrational mode*
A. Bond stretching and valence angle bending coordinates	
A$'$ species	
$S_1 = \frac{1}{\sqrt{3}}(\Delta r_1 + \Delta r_2 + \Delta r_3)$	$\upsilon_s(CD_3)$
$S_2 = \frac{1}{\sqrt{3}}(2\Delta r_1 - \Delta r_2 - \Delta r_3)$	$\upsilon_s'(CD_3)$
$S_3 = \Delta d$	$\upsilon_s(C-C)$
$S_4 = \frac{1}{\sqrt{2}}(\Delta h_1 + \Delta h_2)$	$\upsilon_s(COO)$
$S_5 = \frac{1}{\sqrt{6}}(2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)$	$\delta(COO)$
$S_6 = \frac{1}{\sqrt{6}}(2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)$	$r_s(CD_3)$
$S_7 = \frac{1}{\sqrt{3}}(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3)$	$\delta_s(CD_3)$
$S_8 = \frac{1}{\sqrt{6}}(2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3)$	$\delta_s'(CD_3)$
A$''$ species	
$S_9 = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3)$	$\upsilon_{as}(CD_3)$
$S_{10} = \frac{1}{\sqrt{2}}(\Delta h_2 - \Delta h_3)$	$\upsilon_{as}(COO)$
$S_{11} = \frac{1}{\sqrt{2}}(\Delta\beta_1 - \Delta\beta_2)$	$r_{as}(COO)$
$S_{12} = \frac{1}{\sqrt{2}}(\Delta\phi_2 - \Delta\phi_3)$	$r_{as}(CD_3)$
$S_{13} = \frac{1}{\sqrt{2}}(\Delta\theta_2 - \Delta\theta_3)$	$\delta_{as}(CD_3)$
B. Bond bending coordinates	
A$'$ species	
$S_{14} = \frac{1}{\sqrt{2}}(\Delta\gamma_3 + \Delta\gamma_3')$	$r_s(COO)$
A$''$ species	
$S_{15} = \frac{1}{2}(\Delta\gamma_1' - \Delta\gamma_1'' - \Delta\gamma_3 + \Delta\gamma_3')$	$\tau_{as}(CD_3COO)$, *i.e. torsion about C – C bond*

* ν, stretching mode; δ, deformation mode; *r*, rocking mode; τ, torsional mode; *s*, symmetric; *as*, antisymmetric.

obscure in the $CD_3CO_2^-$ infrared spectrum obtained by Jones and McLaren. Notwithstanding, we obtained a value of about 861 cm^{-1} for it.

Finally, the force field reproduces the observed frequencies very well. The fit is of the same quality for

Table 2: Force constants of the CD_3COO^- ion (x 10^5 dyne cm^{-1})

A. Diagonal Force constants			B. Interaction force constants		
	Coordinate	Value		Coordinates	Value
1.	$\upsilon_{as}(CD_3)$	4.998564	16.	$\upsilon_{as}(CD_3)$ $r_{as}(CD_3)$	0.052865
2.	$\upsilon_s(CD_3)$	5.356283	17.	$\delta_{as}(CD_3)$	0.151815
3.	$\upsilon_s'(CD_3)$	4.930610	18.	$\upsilon_s(CD_3)$ $\upsilon_s(C\text{-}C)$	0.098684
4.	$\upsilon_{as}(COO)$	7.461072	19.	$\Delta_s(CD_3)$	0.153813
5.	$\upsilon_s(COO)$	11.968535	20.	$\upsilon_s'(CD_3)$ $r_s(CD_3)$	0.0528665
6.	$\upsilon_s(C\text{-}C)$	3.094173	21.	$\delta_s'(CD_3)$	- 0.151815
7.	$\delta_{as}(CD_3)$	0.442008	22.	$\upsilon_{as}(COO)$ $r_{as}(COO)$	0.003187
8.	$\delta_s(CD_3)$	1.184269	23.	$\upsilon_s(COO)$ $\delta(COO)$	0.431488
9.	$\delta_s'(CD_3)$	0.426238	24.	$\upsilon_s(C\text{-}C)$ $\upsilon_s(COO)$	0.218297
10.	$r_{as}(CD_3)$	0.351014	25.	$\delta(COO)$	0.033260
11.	$r_s(CD_3)$	0.343804	26.	$\delta_s(CD_3)$	0.142183
12.	$\delta(COO)$	0.138025	27.	$r_{as}(CD_3)$ $\delta_{as}(CD_3)$	0.030968
13.	$r_{as}(COO)$	0.178017	28.	$r_s(CD_3)$ $\delta_s'(CD_3)$	-0.030968
14.	$r_s(COO)$	1.040023	29.	$\delta(COO)$ $r_s(CD_3)$	-0.006175
15.	$\tau_{as}(CD_3COO)$	1.565567	30.	$r_{as}(COO)$ $r_{as}(CD_3)$	0.018525

Table 3: Comparison of calculated and observed frequencies (cm^{-1}) in $CD_3CO_2^-$ ion.

Species	Obs. Freq.*	Calc. Freq.	Assignment	CMUV**
			A. Bond stretching and valence angle bending vibrations	
$A^{/}$				
υ_1	2183	2182.61	$\upsilon_s(CD_3)$	~99.94%
υ_2	2254	2254.37	$\upsilon^{/}_s(CD_3)$	~99.99%
υ_3	928	929.47	$\upsilon_s(C\text{-}C)[96.17\%]+\upsilon_s(COO)[1.22\%]$ $+\delta_s(CD_3)[2.17\%]$	~99.56%
υ_4	1406	1408.17	$\upsilon_s(COO)$	~99.92%
υ_5	609	608.46	$\delta(COO)[84.53\%]+\upsilon_s(COO)[13.68\%]$ $+\delta_s(CD_3)[1.16\%]$	~99.37%
υ_6	880	880.89	$r_s(CD_3)[91.49\%]+\delta_s(CD_3)[1.29\%]+\delta'_s(CD_3)[5.79\%]$	~98.57%
υ_7	1030	1032.49	$\delta_s(CD_3)[83.58\%] + \upsilon_s(C\text{-}C)[15.37\%]$	~98.95%
υ_8	1081	1086.09	$\delta^{/}_s(CD_3)[93.25\%]+\upsilon'_s(CD_3)[1.47\%]$ $+ r_s(CD_3)[3.99\%]+\delta_s(CD_3)[1.20\%]$	~99.91%
$A^{//}$				
υ_9	2167	2163.46	$\upsilon_{as}(CD_3)$	~99.99%
υ_{10}	1563	1565.46	$\upsilon_{as}(COO)$	~99.99%
υ_{11}	411	408.11	$r_{as}(COO)$	~99.78%
υ_{12}	828	8280.00	$r_{as}(CD_3)[94.30\%]+ \delta_{as}(CD_3)[5.11\%]$	~99.41%
υ_{13}	1045	1045.53	$\delta_{as}(CD_3)[95.26\%]+ \upsilon_{as}(CD_3)[1.46\%]$ $+ r_{as}(CD_3)[3.28\%]$	~100%
			A. Bond bending vibrations	
$A^{/}$				
υ_{14}	525	525.00	$r_s(COO)$	~100%
$A^{//}$				
υ_{15}	-	861.00	$\tau_{as}(CD_3COO)$	~100%

* Taken from ref. 1.** CMUV = combination making up to ………………. of vibration.

Table 4: Force constants (x 10^5 dyne cm^{-1}) for some groups in the $CD_3CO_2^-$ ion compared with values known for closer molecules

Coordinates	Value $CH_3COOCH_3^a$	 $CH_3COCH_3^b$	 $CD_3CO_2^-$ ion
$\upsilon_{as}(CD_3)$	4.8150		4.998564
$\upsilon_s(CD_3)$	5.1050		5.356283
$\upsilon'_s(CD_3)$	4.9018		4.930610
$\upsilon(C\text{-}C)$	4.6377^b	4.077	3.094173
$\delta_{as}(CD_3)$	0.4596		0.442008
$\delta'_s(CD_3)$	0.4563		0.426238
$r_{as}(CD_3)$	0.7310	0.406	0.351014
$r_s(CD_3)$	0.7252	0.406	0.343804
$r_s(CD_3)$ $\delta'_s(CD_3)$	-0.0226		-0.030968

[a] Taken from ref. 6; [b] taken from ref.

Table 5: Jacobian matrices for diagonal force of $CD_3CO_2^-$ ion

Coord-inate	$\upsilon_s(CD_3)$	$\upsilon'_s(CD_3)$	$\upsilon_s(C\text{-}C)$	$\upsilon_s(COO)$	$\delta(COO)$	$r_s(CD_3)$	$\delta_s(CD_3)$	$\delta'_s(CD_3)$	$\upsilon_{as}(CD_3)$	$\upsilon_{as}(COO)$	$r_{as}(COO)$	$r_{as}(CD_3)$	$\delta_{as}(CD_3)$	r_s(COO
λ_1	0.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00						
λ_2	0.00	0.99	0.00	0.00	0.00	0.00	0.00	0.00						
λ_3	0.00	0.00	0.93	0.00	0.00	0.00	0.06	0.00						
λ_4	0.00	0.00	0.00	0.99	0.00	0.00	0.00	0.00						
λ_5	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.00						
λ_6	0.00	0.00	0.00	0.00	0.00	0.94	0.00	0.05						
λ_7	0.00	0.00	0.07	0.00	0.00	0.00	0.92	0.00						
λ_8	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.94						
λ_9									0.99	0.00	0.00	0.00	0.00	
λ_{10}									0.00	1.00	0.00	0.00	0.00	
λ_{11}									0.00	0.00	0.99	0.00	0.00	
λ_{12}									0.00	0.00	0.00	097	0.02	
λ_{13}									0.00	0.00	0.00	0.02	0.97	
λ_{14}														1.00

the CD_3-C fragment of the $CD_3CO_2^-$ ion as those obtained for the same fragment in the CH_3COOCH_3 [6] and CH_3COCH_3 [5] molecules. In Table 4 the CH_3COOCH_3, CH_3COCH_3 and $CD_3CO_2^-$ ion force constants for this fragment are listed. Comparing the values given in this table, almost all the force constants agree satisfactorily. This agreement indicates that the transfer of the CD_3-C fragmental force constants from the CH_3COOCH_3 and CH_3COCH_3 molecules to $CD_3CO_2^-$ ion was quite reasonable.

Lastly, in order to investigate the sensitivity of each normal frequency to the value of each force constant, the Jacobian matrix [10], given in Table 5, was calculated. This matrix was used to adjust the force field to the observed frequencies. As shown in this table, CD_3 rocking absorption bands are sensitive to changes in the force constant of CD_3 deformation vibrations. The same conclusion may also be drawn about the CD_3 deformation bands and C-C stretching and CD_3 rocking force constants.

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