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Infrared and Raman Spectra of *S*-Methyl Thioacetate: Toward an Understanding of the Biochemical Reactivity of Esters of Coenzyme A[†]

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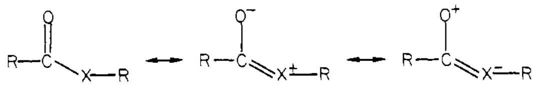
ABSTRACT: The infrared and Raman spectra of *S*-methyl thioacetate and $CD_3C(O)SCH_3$ have been determined. These spectra and those in the literature for *S*-ethyl thioacetate have been assigned. These data together with literature assignments for thioformic acid, thioacetic acid, and *S*-methyl thioformate were used in normal coordinate calculations. The stretching force constant for the carbonyl group of thioesters and thio acids is found to be very similar to that for the carbonyl group of ketones. In addition, the value of the stretching force constant for the C(O)–S bond in thioesters and thio acids indicates that this entity has no double-bond character. The carbonyl group of acetyl coenzyme A is essentially the same as that of a ketone.

The biochemical importance of coenzyme A and its acyl derivatives (Gregory & Lipmann, 1952) has led to a continuing interest in thioesters. These molecules have low carbonyl stretching frequencies, similar to those of amides, but the hydrogen-bond acceptor basicity of the carbonyl oxygen of a thioester is significantly lower than that of an amide (Baker & Harris, 1960).

Baker and Harris proposed an explanation for these properties that invoked resonance structures I–III, in which X is



I II III

sulfur. Structure III implies $(2p{-}3d)_\pi$ bonding that is im-

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Table I: Infrared and Raman Spectra of Liquid *S*-Methyl Thioacetate^a

IR (cm^{-1})	Raman (cm^{-1})	designation^b	assignment^c	calcd (cm^{-1})
	230 (m, p)	ν_{17}	def	223
359 (m)	359 (m, p)	ν_{16}	def	352
425 (m)		ν_{24}	CO opb	
440 (w)		ν_{17}		
493 (w)	492 (s, p)	ν_{15}	def	490
531 (w)	530 (w, dp)	?		
626 (vs)	628 (vs, p)	ν_{14}	C(O)–S st	628
726 (m)	728 (s, p)	ν_{13}	S–CH_3 st	728
940 (m)	940 (w, dp)	ν_{23}	(S)–CH_3 r	
988 (m)	987 (m, p)	ν_{12}	(C)CH_3 r	983
	1066 (w, dp)	ν_{22}	(C)CH_3 r	
1106 (m)	1108 (m, p)	ν_{11}	(S)CH_3 r	1109
1140 (s)	1137 (m, p)	ν_{10}	C–C st	1126
1218 (vw)		$\nu_{13} + \nu_{15}$		
1250 (vw)		$2\nu_{14}$		
1312 (m)	1313 (m, p)	ν_9	(S)CH_3 sb	1312
1355 (s)	1355 (m, p)	ν_8	(C)CH_3 sb	1357
1428 (m)	1430 (m, dp)	ν_6, ν_{20}	(S)CH_3 ab	
		ν_7, ν_{21}	(C)CH_3 ab	
1690 (vs)	1692 (s, p)	ν_5	C=O st	1692
1840 (vw)		$\nu_{11} + \nu_{13}$		
1910 (vw)		$\nu_6 + \nu_{15}$		
2250 (vw)		$\nu_9 + \nu_{23}$		
2345 (vw)		$\nu_8 + \nu_{12}$		
2485 (vw)		$\nu_8 + \nu_{10}$		
2625 (vw)		$2\nu_9$		
2830 (m)	2833 (m, p)	$2\nu_6$		
2929 (vs)	2930 (vs, p)	ν_3, ν_4	(S, C)CH_3 ss	2931
3003 (s)	3006 (s, dp)	ν_1, ν_{18}	(S)CH_3 as	3009
		ν_2, ν_{19}	(C)CH_3 as	3007
3375 (m)		$2\nu_5$		

^{a} w = weak, vw = very weak, m = medium, s = strong, vs = very strong, p = polarized, and dp = depolarized. ^{b} Combination bands based on observed fundamentals and harmonic behavior. ^{c} def = skeletal deformation, opb = out of plane bend, st = stretch, r = rock, sb = symmetric bend, ab = asymmetric bend, ss = symmetric stretch, and as = asymmetric stretch.

Table II: Infrared and Raman Spectra of Liquid *S*-Methyl Thioacetate-d_3 ^{d}

IR (cm^{-1})	Raman (cm^{-1})	designation	assignment	calcd (cm^{-1})
	222 (m, p)	ν_{17}	def	218
335 (m)	330 (s, p)	ν_{16}	def	328
425 (m)		ν_{24}	CO opb	
484 (m)	482 (m, p)	ν_{15}	def	476
573 (s)	573 (vs, p)	ν_{14}	C(O)–S st	577
623 (sh)	623 (w, p)	?		
724 (m)	723 (s, p)	ν_{13}	S–CH_3 st	724
812 (m)	810 (m, p)	ν_{12}	(C)CH_3 r	806
854 (w)		ν_{22}	(C)CH_3 r	
	962 (sh, ?)	ν_{23}	(S)CH_3 r	
990 (s)	988 (m, p)	ν_8	(C)CH_3 sb	984
1034 (sh)	1034 (w, p)	ν_7, ν_{21}	(C)CH_3 ab	
	1103 (vw)	?	(S)CH_3 r	1109
1150 (s)	1150 (w, p)	ν_{10}	C–C st	1148
1262 (w)		$\nu_{13} + \nu_{14}$		
1315 (m)	1314 (m, p)	ν_9	(S)CH_3 sb	1312
1426 (m)	1427 (m, dp)	ν_6, ν_{20}	(S)CH_3 ab	
1560 (vw)		$\nu_{13} + \nu_{22}$		
1690 (vs)	1686 (s, p)	ν_5	C=O st	1686
1800 (vw)		$\nu_8 + \nu_{12}$		
1950 (vw)		$2\nu_8$		
2030 (vw)		$\nu_7 + \nu_8$		
	2051 (w, p)	$2\nu_7$		
2103 (w)	2103 (s, p)	ν_4	(C)CH_3 ss	2108
2145 (vw)	2144 (m, p)	$\nu_8 + \nu_{10}$		
2250 (w)	2250 (m, dp)	ν_2, ν_{19}	(C)CH_3 as	2250
2832 (w)	2832 (w, p)	$2\nu_6$		
2932 (s)	2931 (s, p)	ν_3	(S)CH_3 ss	2931
3010 (w)	3010 (m, dp)	ν_1, ν_{18}	(S)CH_3 as	3009

^{a} sh = shoulder. All other symbols are defined in the footnotes to Table I.

possible when X is nitrogen or oxygen. The Baker and Harris proposal is, however, inconsistent with Wadsö's (1962) finding that the resonance energies of thioesters are smaller than those of oxygen esters by some 13 kcal·mol^{-1}. In addition, whereas Baker and Harris adopted the assignment of Mecke & Luttringhaus (1957) and placed the C(O)–S stretching frequency of thioesters in the range 900–1000 cm^{-1}, subsequent studies by Collings et al. (1970) and Crowder (1972) suggest that this vibration actually occurs in the 600–700-cm^{-1} range cited by Sheppard (1950) as characteristic of the C–S linkage in alkyl mercaptans, sulfides, and disulfides. A C(O)–S vibration in the latter region would imply that structures II and III are of little or no importance in the ground state of thioesters.

This study was undertaken to obtain additional information relating to the question of resonance in the ground state of thioesters. We have measured and assigned the infrared and Raman spectra of $CH_3C(O)SCH_3$ and $CD_3C(O)SCH_3$ and assigned the literature infrared and Raman spectra of $CH_3C(O)SC_2H_5$ (Sadtler Research Laboratories, 1975; Texas A&M TRC, 1977). This information, together with the literature frequencies and assignments for thioformic acid (Engler & Gattow, 1972), *S*-methyl thioformate (Jones et al., 1976), and thioacetic acid (Crowder et al., 1975), was used in normal coordinate calculations encompassing all six molecules.

Materials and Methods

Syntheses. *S*-Methyl thioacetate was prepared by the direct reaction of acetyl chloride with methanethiol (Arndt et al., 1939). The crude ester was purified by gas–liquid chromatography (GLC). We prepared $CD_3C(O)SCH_3$ in a similar manner after first having prepared acetyl-d_3 chloride from acetic acid-d_4. A mass spectrum showed the isotopic purity of the resulting ester to be about 99%.

Spectroscopic Measurements. Infrared spectra of thin films of the pure liquid thioesters held between KBr plates at ambient temperature were recorded in the 300–3400-cm^{-1} region with a Beckman IR-12 spectrophotometer. Vapor spectra were obtained by evaporating a few drops of each liquid in a 10-cm gas cell.

Raman spectra of the pure liquids sealed in glass capillaries were excited by the 488-nm argon ion line of a Spectra-Physics Model 164-02 laser operated at 50–200 mW. The spectra were recorded with a Spex Ramalab spectrometer operated in the photon-counting mode. The frequency accuracy of both the infrared and the Raman spectra is ±3 cm^{-1}.

Spectroscopic Results. The experimental spectra are listed and assigned in Table I for *S*-methyl thioacetate and Table II for *S*-methyl thioacetate-d_3. The Raman polarization data strongly suggest C_s symmetry, under which the 27 normal modes are distributed 17 A′ plus 10 A″. Thus, in Tables I and II the vibrations with A′ symmetry are numbered ν_1–ν_{17}, and those with A″ symmetry are numbered ν_{18}–ν_{24}. Three low-frequency torsions of A″ symmetry were not observed.

The proposed assignments are based on well-established group frequencies, supplemented by the Raman polarization data and isotope shifts that serve mainly to distinguish (C)CH_3 motions from (S)CH_3 motions. Where applicable, we have also adopted the assignments of Collings et al. (1970) and Crowder (1972).

Normal Coordinate Calculations. (*A*) *Structural Parameters.* Structural data were available in the literature for thioformic acid (Hocking & Winnewisser, 1976), *S*-methyl

Table III: Distribution of Normal Modes of Thioesters and Thio Acids

compd	A′ vibrations total	A′ vibrations obsd	A″ vibrations total	A″ vibrations obsd
thioformic acid	7	6	2	1
thioacetic acid	12	12	6	4
S-methyl thioformate	12	12	6	4
S-methyl thioacetate	17	17	10	7
S-ethyl thioacetate	22	21	14	8

Table IV: Symmetry Force Constants for the A′ Vibrations of Thioesters and Thio Acids[a]

Diagonal Force Constants

force constant	symmetry coordinate[b] description	value[c]	applies to[d]
F1	(S)CH_3 ss	4.951 (13)	MTA, MTF
F2	(CO)CH_3 ss	4.939 (12)	MTA, TA, ETA
F3	(CH_2)CH_3 ss	4.775 (C)	ETA
F4	CH_2 ss	4.638 (30)	ETA
F5	(S)CH_3 as	4.810 (12)	MTA, MTF
F6	(CO)CH_3 as	4.796 (15)	MTA, TA, ETA
F7	(CH_2)CH_3 as	4.690 (22)	ETA
F8	C(O)-H st	4.383 (15)	MTF, TF
F9	S-H st	3.726 (14)	TA, TF
F10	S-$CH_{2,3}$ st	3.100 (41)	MTA, ETA, MTF
F11	C(O)-S st	2.975 (129)	all
F12	C-C(O) st	4.88 (C)	MTA, ETA, TA
F13	C-C st	4.175 (92)	ETA
F14	C=O st	9.766 (82)	all
F15	(S)CH_3 sb	0.544 (3)	MTA, MTF
F16	(CO)CH_3 sb	0.576 (4)	MTA, ETA, TA
F17	(C)CH_3 sb	0.584 (6)	ETA
F18	(S)CH_3 ab	0.487 (4)	MTA, MTF
F19	(CO)CH_3 ab	0.507 (3)	MTA, ETA, TA
F20	(C)CH_3 ab	0.501 (6)	ETA
F21	CH_2 sci	0.557 (6)	ETA
F22	CH_2 wag	0.592 (8)	ETA
F23	(S)CH_3 r	0.872 (10)	MTA, MTF
F24	(CO)CH_3 r	0.623 (19)	MTA, ETA, TA
F25	(C)CH_3 r	0.703 (13)	ETA
F26	OCS b	0.967 (44)	all
F27	CC(O)S b	1.675 (119)	MTA, ETA, TA
F28	SCC b	1.142 (88)	ETA
F29	(O)SCS b	1.504 (86)	MTA, ETA, MTF
F30	HCO b	0.643 (7)	MTF, TF
F31	(O)CSH b	0.754 (11)	TA, TF

Interaction Force Constants

force constant	value	force constant	value[e]
F12,16	−0.632 (25)	F10,15	−0.425 (T)
F12,24	−0.407 (34)	F13,17	−0.358 (T)
F24,26	−0.159 (44)	F11,12	0.39 (C)
F11,26	0.219 (31)	F10,13	0.512 (T)
F12,26	−0.958 (86)	F13,28	0.210 (T)
F12,27	1.082 (50)	F13,22	0.083 (T)
F10,28	0.674 (105)	F10,22	−0.288 (T)
F11,30	0.208 (42)	F10,21	−0.183 (T)
F11,31	0.461 (28)	F13,21	−0.158 (T)

[a] Stretching constants are in units of $\text{mdyn}\cdot\text{Å}^{-1}$; bending constants are in units of $\text{mdyn}\cdot\text{Å}\cdot\text{rad}^{-2}$; stretch–bend interaction constants are in units of $\text{mdyn}\cdot\text{rad}^{-1}$. [b] ss = symmetric stretch, as = asymmetric stretch, st = stretch, sb = symmetric bend, ab = asymmetric bend, sci = scissors, r = rock, and b = bend. [c] Numbers in parentheses are the standard errors in the last significant digits. Force constants marked by (C) were contained during the refinements. [d] MTA = *S*-methyl thioacetate, MTF = *S*-methyl thioformate, TA = thioacetic acid, ETA = *S*-ethyl thioacetate, and TF = thioformic acid. [e] Force constants marked by (T) were transferred; see the text.

thioformate (Jones et al., 1976), and thioacetic acid (Gordy, 1946). For *S*-methyl thioacetate and *S*-ethyl thioacetate, the structural parameters were assumed to be similar to those found in thioacetic acid and *S*-methyl thioformate. Tetrahedral bond angles were assumed for the methylene carbon of the ethyl group. On the basis of the results of a dipole-moment study by Hirabayashi (1965), we further assumed that in the thioesters the S–R group is cis to the carbonyl group.

(*B*) *Calculations.* We performed normal coordinate calculations using the GF-matrix method on a Burroughs B6700 computer using the Schachtschneider (Schachtschneider & Snyder, 1963; Schachtschneider, 1964, 1965) program package. A symmetrized valence force field was employed.

In C_s symmetry the in-plane (A′) and out-of-plane (A″) motions are distributed as shown in Table III. Shimanouchi (1970) suggested that the potential constants associated with the $-CH_3$ and –C(O)O– groups may be transferable among molecules with similar structures. We assume that the constants for the $-CH_3$ and –C(O)S– groups are transferable. With this assumption, the six molecules provided a total of 85 observed frequencies for normal modes with A′ symmetry and 31 observed frequencies for normal modes with A″ symmetry.

Within each symmetry block, an initial set of diagonal force constants was chosen mainly on the basis of values given by Crowder et al. (1975) and Scott & El-Sabban (1969). Interaction constants were then added one by one until a set of trial force constants was obtained for which the calculated potential energy distributions were in reasonable agreement with the various "experimental" assignments. This trial force field was then subjected to least-squares refinements. All observed frequencies were assigned ν^{-2} (observed) weights; unobserved frequencies were given zero weight. During the refinement process a few additional interaction constants were introduced in order to optimize the overall frequency fit.

Computational Results. Since the focus of this paper is on the in-plane carbonyl stretching frequencies of thioesters, we report here only results for the A′ symmetry block. A full set of results, including the force constants for the A″ block and tables of the observed and calculated wavenumbers for all the vibrations of all six molecules, is available elsewhere (El-Aasar, 1979).

Table IV lists the final symmetry force constants for the A′ symmetry block together with their standard errors. The tabulated symmetry force constants are identical with valence force constants in seven cases: the C(O)–H stretch (F8); the S–H stretch (F9); the S–CH_3 stretch (F10); the C(O)–S stretch (F11); the C–C(O) stretch (F12); the H_3C–CH_2 stretch (F13); the C=O stretch (F14).

For the A′ symmetry block there are 49 evaluated force constants, 31 diagonal, and 18 off-diagonal. Constants F3, F12, and F11,12 were constrained during the least-squares refinements. The eight interaction constants marked with a (T) in Table IV are associated with the S–CH_2–CH_3 group in *S*-ethyl thioacetate and were obtained from the force field for thioalkanes and alkanethiols found by Scott & El-Sabban (1969), suitably transformed from valence coordinates to symmetry coordinates. These force constants were also held fixed during the refinement process.

The largest off-diagonal elements in the final force field represent stretch–bend interactions in the H_3C–C(O)–S group. In their vibrational analysis of thioacetic acid Crowder et al. (1975) also found these interactions to be quite significant. We also agree with these authors' finding of a considerable interaction between the C(O)–S stretching and C–S–H bending modes, F11,31. Most of the remaining interaction force constants are ones that are known to be important in molecules containing X–CH_3 groups (King et al., 1957; Aldous & Mills, 1962).

The force field given in Table IV reproduces the 85 observed frequencies of the six molecules on which it is based with an overall average error of 3.7 cm^{-1}. Such agreement suggests that this set of force constants is acceptably transferable.

The last column in Tables I and II contains the wavenumbers calculated for the 17 A′ vibrations with the force constants in Table IV. The calculations reproduce the observed frequencies to within an average error of 2.9 cm^{-1} for *S*-methyl thioacetate and 2.5 cm^{-1} for *S*-methyl thioacetate-d_3. Our principal interest is in the carbonyl frequencies for which the calculated values are exactly the same as those observed in the Raman spectra of the two pure liquids.

An unexpected qualitative result of the spectroscopic experiments was the observation that the thioester band near 625 cm^{-1}, assigned by Collings et al. (1970) and Crowder (1972) to the C(O)–S stretching vibration, shifted appreciably when the acetyl carbon was deuterated. The calculated potential energy distribution for this normal mode [45% C–S stretch; 30% C(O)–CH_3 rock; 20% C–C stretch] shows that it is, in fact, a highly mixed motion.

Discussion

The primary intent of this work was to determine if the low vibration frequency of the carbonyl group of thioesters is a consequence of a (relatively) small force constant indicative of electron delocalization in the C=O bond. A comparison of carbonyl force constants is somewhat complicated by the fact that the C=O vibration frequency is quite sensitive to the environment of the molecule. The carbonyl frequency of acetone shifts from 1738 cm^{-1} in the gas phase (Cossee & Schachtschneider, 1966) to 1707 cm^{-1} in the neat liquid (Fouassier & Forel, 1972). Similar results are found for methyl acetate [1771 → 1740 cm^{-1} (George et al., 1974)], for *N*-methylacetamide [1718 → 1653 cm^{-1} (Miyazawa et al., 1956)], and for *S*-methyl thioacetate [1720 → 1692 cm^{-1} (this work)]. Since the biological interest in thioesters concerns their behavior in polar solution, for which the pure liquid is not a wholly unrealistic approximation, we have elected to compare the carbonyl force constants for the listed molecules in their pure liquid states.

A valence force field for liquid acetone has been published by Fouassier & Forel (1972), who report a carbonyl stretching force constant of 9.57 mdyn·$Å^{-1}$. This value is quite reasonable when compared to the gas-phase value of 9.72 mdyn·$Å^{-1}$ calculated by Cossee & Schachtschneider (1966).

We have used the frequency data of George et al. (1974) for three hydrogen isotopic variants of methyl acetate to establish a symmetrized valence force field for this molecule also (El-Aasar, 1979). We find a gas-phase carbonyl force constant of 11.69 mdyn·$Å^{-1}$, in excellent agreement with the value of 11.60 mdyn·$Å^{-1}$ found in a less elaborate calculation by Matzke et al. (1971). We further find from an examination of the **JZ** matrix that the liquid-state frequency of methyl acetate can be reproduced if the carbonyl force constant is reduced to 11.2 mdyn·$Å^{-1}$.

Two different valence force fields for *N*-methylacetamide in the liquid state give virtually identical carbonyl force constants. Jakes & Krimm (1971) report 8.78 mdyn·$Å^{-1}$, while Rey-Lafon et al. (1973) report 8.9 mdyn·$Å^{-1}$.

For liquid *S*-methyl thioacetate we find a force constant of 9.77 mdyn·$Å^{-1}$ and compute also that a constant of 10.3 mdyn·$Å^{-1}$ will reproduce the gas-phase frequency.

When all four molecules are compared in the liquid state, we find carbonyl stretching force constants that increase in the order *N*-methylacetamide < acetone ≥ *S*-methyl thioacetate < methyl acetate. This order differs slightly from the order of observed carbonyl frequencies, since in either the gas or the liquid phases acetone absorbs at about 15-cm^{-1} higher energy than the thioester.

This difference may be rationalized on the basis of model calculations by Collings et al. (1970), which show clearly that the carbonyl frequency is sensitive to molecular features other than just $F_{C=O}$. These authors found that for the simple system of four point masses, M–C(O)–X, the highest calculated frequency decreased from 1768 to 1745 cm^{-1} as the result of three changes in the model parameters, all others being held constant. The mass of X was increased from 16 to 32; the C–X distance was increased from 1.22 to 1.78 Å; F_{C-X} was decreased from 4.8 to 3.1 mdyn·$Å^{-1}$. Apart from the change in bond length, these changes collectively should fairly well represent the changes that occur when a CH_3 group of acetone is replaced by an S–CH_3 group. The distance change is too large, but this change taken by itself contributes only 6–7 cm^{-1} to the total decrease in the calculated frequency.

The potential energy distributions for the carbonyl frequencies of acetone and the thioesters reveal much the same picture. Methyl rocking, C–C stretching, and C–C(O)–C angle-bending motions each contribute between 10 and 15% to the observed carbonyl frequency of acetone (Cossee & Schachtschneider, 1966), whereas only the angle-bending motion is of comparable significance for the thioester.

Our finding that the carbonyl stretching force constants of ketones and thioesters are very similar provides yet another entry in the growing list of chemical and physical similarities shared by these classes of compounds. They have similar α-proton acidities, their group migratory aptitudes are comparable, both are easily reduced by sodium borohydride, and the carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra of thioesters resemble those of ketones far more than they do those of acids, O esters, or amides (Hall & Wemple, 1977, and references cited therein).

Since the carbonyl stretching force constants of ketones and thioesters are nearly the same, we infer that neither structure II nor structure III makes a significant contribution to the ground state of thioesters. In the absence of resonance effects, groups with similar electronegativities have similar influences on the carbonyl vibration frequency (Kagarise, 1955), and the electronegativities of an alkyl group and an SR group should be almost identical (Hinze & Jaffe, 1962).

Further support for this view may be found in the fact that the force constants for the C(O)–S and the S–R bonds in thioesters are the same within their estimated standard errors. In both oxygen esters and amides, where significant resonance effects are known to be present, the C(O)–X force constant is larger than the X–R force constant by 15–25% (Matzke et al., 1971; Jakes & Krimm, 1971; Rey-Lafon et al., 1973).

The function of the sulfur in acetyl coenzyme A and other coenzyme A esters becomes clear from this and also from previous chemical studies. The negligible amount of normal ester-like resonance allows acetyl coenzyme A to possess a driving force for acetylation reactions to form oxygen esters or amides with large resonance stabilizations and for the formation of α carbanions because the carbonyl oxygen is a much better electron sink than that in oxygen esters. This is the result of the lack of resonance rather than sulfur d-orbital expansion. The carbonyl group of acetyl coenzyme A is thus very similar to that of a ketone.

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