An analysis of the methyl rotation dynamics in the S0 (1A1) and T1 (3A2) states of thioacetone, (CH3)2CS and (CD3)2CS from pyrolysis jet spectra

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An analysis of the methyl rotation dynamics in the S_0 ($\tilde{X}\,^1A_1$) and T_1 ($\tilde{a}\,^3A_2$) states of thioacetone, $(CH_3)_2CS$ and $(CD_3)_2CS$ from pyrolysis jet spectra

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Jet-cooled, laser-induced phosphorescence excitation spectra (LIP) of thioacetone $(CH_3)_2CS/(CD_3)_2CS$ have been recorded over the region 16 800–18 500 cm^{-1} using the pyrolysis jet spectroscopic technique. The responsible electronic transition, $T_1 \leftarrow S_0$, $\tilde{a}\,^3A'' \leftarrow \tilde{X}\,^1A_1$, results from an $n \rightarrow \pi^*$ electron promotion and gives rise to a pattern of vibronic bands that were attributed to activity of the methyl torsion and the sulphur out-of-plane wagging modes. The intensities of the torsional and wagging progressions in the excitation spectra were interpreted in terms of a C_{2v}–C_s molecular distortion of the triplet molecule from its singlet ground state equilibrium structure. A complete unrestricted Hartree–Fock (UHF) *ab initio* molecular orbital (MO) structural optimization of the T_1 state predicted that the sulphur was displaced by 27.36° from the molecular plane and the methyl groups were rotated by 10.93° in clockwise–counterclockwise directions. Restricted Hartree–Fock (RHF) calculations were used to generate the $V(\theta_1, \theta_2)$ potential surface governing methyl rotation for the S_0 state. This was incorporated into a two-dimensional Hamiltonian, symmetrized for the G_{36} point group and solved variationally for the torsional frequencies. The calculated frequencies of 159.97/118.94 for the ν_{17} (b_1) mode of S_0 $(CH_3)_2CS/(CD_3)_2CS$ were found to agree with the experimental values, 153.2/114.7 cm^{-1}.

INTRODUCTION

Experimental information about the dynamics of methyl internal rotation has come from the analyses of weak bands in the far infrared and Raman spectra.[1] Internal rotation has also been studied from a theoretical point of view[2] and the potential surfaces governing the large amplitude motions have been calculated directly by *ab initio* molecular orbital procedures.

Visible or ultraviolet (UV) spectra, which result from transitions between ground and excited electronic states, contain information about the vibrational motions of both electronic states. For the ground state, these data may come from the hot band vibrational structure which arises from transitions which connect the thermally populated vibrational levels of the ground electronic state with the levels of the upper state. As the band intensities in electronic spectra are controlled by Franck–Condon overlap considerations it follows that this information will be different from that obtained by infrared or Raman spectroscopies. This is particularly true for the case where the methyl groups adopt different conformations in the two combining electronic states.

UV–visible absorption spectra of thioacetone vapor have been reported previously.[3,4] Under conditions of low resolution and long path length, two systems were observed in the 500–600 nm region which were assigned as $n \rightarrow \pi^*$ excitations to the first triplet T_1 ($\tilde{a}\,^3A_2$) and first singlet S_1 ($\tilde{A}\,^1A_2$) excited states. The T_1 state is phosphorescent[5] with a collision-free lifetime of 10 μs. The $T_1 \leftarrow S_0$ excitation and absorption spectra consist of highly congested band clusters which were assigned to the activity of the methyl torsion modes.

An insight into the possible complexities of the excited state vibrational dynamics of thioacetone can be found in the recent analysis of the absorption spectrum of thioacetaldehyde,[6,7] CH_3CHS, where it was shown that, on excitation, the methyl group rotates from an eclipsed to a staggered configuration while at the same time, the aldehyde hydrogen distorts from the plane. Thus, the low frequency dynamics of T_1 thioacetaldehyde are dominated by two large amplitude modes: a torsion of the methyl group and a wagging-inversion of the molecular frame. In thioacetone, an additional complication comes from the second methyl group. Thus, an understanding of the low frequency dynamics of the T_1 state of thioacetone requires the solution to a vibrational Hamiltonian which depends on three large amplitude modes.

The situation for the S_0 state is somewhat less complex. Kroto *et al.*[8,9] have obtained a partial molecular structure for thioacetone from its microwave spectrum. Their analyses showed that the CCCS atoms form a rigid planar framework with the in-plane hydrogens of the methyl group in an eclipsed conformation with respect to the sulphur atom. From the splitting pattern among the microwave line satel-

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lites they were able to estimate an effective barrier to internal methyl rotation of 455 cm^{-1}. As a result of molecular instability with respect to polymerization, the infrared spectrum of thioacetone vapor has not been recorded although a liquid phase spectrum has been reported.[10]

The purpose of this work is to obtain a description of the low frequency dynamics of the two methyl groups in S_0 electronic ground state of thioacetone. This is achieved by combining the energy level data extracted from the intervals observed in warm supersonic jet spectra with the levels derived by solving the torsional Hamiltonian in two dimensions. We have recently considered thioacetone from the viewpoint[11] of a semirigid model with unrelaxed geometry. The new data presented here revises our earlier assignment. The pyramidal distortion of the thiocarbonyl group in the T_1 excited state which results from $n \rightarrow \pi^*$ excitation leads to the creation of a large amplitude sulphur wagging mode. Thus, it would require three coordinates to describe the large amplitude motions: wagging plus double methyl internal rotation. The solution to this three-dimensional problem is beyond the scope of the present work. It is possible, however, to use the unrestricted Hartree–Fock (UHF) scheme to locate an optimized equilibrium structure and the harmonic vibrational frequencies for the upper state. Such information is invaluable in assigning the band spectra.

EXPERIMENT

Thioketones can be synthesized as red colored liquids, which are unstable at room temperature and polymerize to form the colorless cyclic trimer. For this reason they are best generated and detected in a flow system. In this case the trimer, hexamethyl-s-trithiane, was prepared by the method of Kroto *et al.*[8] from HCl, H_2S, and $(CH_3)_2CO$. For thioacetone-*d* 6, fully deuterated compounds were used.

Jet-cooled phosphorescence excitation spectra of thioacetone and thioacetone-d_6 were obtained using the pyrolysis jet spectroscopic technique described elsewhere.[12] The liquid trimer was warmed to 50 °C, the vapor entrained in 1 atm of argon, and the mixture pyrolyzed at 700 °C just prior to expansion through a 150 μm nozzle into vacuum. From past experience we estimate that rotational temperatures of 5–10 K were obtained under these conditions. In order to accentuate the weak hot bands, warm jet spectra were also recorded by altering the expansion conditions to prevent complete cooling of molecules in higher vibrational levels populated in the high temperature pyrolysis zone.

The phosphorescence of thioacetone was excited with a Nd:YAG pumped dye laser system (Lumonics HY 750 + HyperDye 300) using Rhodamine 6G, Rhodamine 610, and Coumarin 540A laser dyes (Exciton). Laser powers of 1–5 mJ/pulse and linewidths of ~ 0.1 cm^{-1} were employed. The emission was detected by imaging the cold portion of the supersonic expansion through a suitable cutoff filter to reject scattered light and onto a high gain, red sensitive photomultiplier (EMI 9816 QB). The excitation spectra were wavelength calibrated by simultaneously observing the optogalvanic effect in a neon filled hollow cathode lamp.

Wavelength calibrated and laser power corrected spectra were obtained by simultaneously recording the phospho-

rescence excitation spectrum, optogalvanic spectrum, and laser power on a computerized data acquisition of our own design.[13] The pulsed signals were processed by gated integrators prior to digital acquisition.

For the absorption studies, the products of the pyrolysis were passed directly into a 2 m White-type multiple reflection cell set for a path length of 98 m. The best spectra were recorded at a pressure of 2 Torr. Medium resolution spectra were recorded on a Bausch and Lomb 1.5 m grating spectrograph at a dispersion of 15 nm/cm. A 450 W Xe arc was used as a continuum source of radiation and emission lines from a Fe–Ne hollow cathode lamp served as references.

RESULTS AND ASSIGNMENTS

Figure 1 compares a microdensitometer tracing of the visible spectrum of thioacetone $(CH_3)_2CS$ photographed at long path length in absorption with the excitation spectrum recorded under supersonic jet conditions. Listings of the observed band heads in the excitation spectra are given in Tables I and II. It is obvious that the absorption spectrum is highly congested and that it simplifies dramatically with jet cooling.

The electronic 0_0^0 origin of the singlet–triplet system can be identified without difficulty as the moderately intense bands in the $(CH_3)_2CS/(CD_3)_2CS$ spectra at 17 327.8/17 349.8 cm^{-1}. The warm temperature jet spectra of Figs. 2 and 3, which extend to lower wave numbers from the origin, provide the starting point for the assignment of the vibrational band structure. These spectra display short band progressions which may be assigned to vibrational activity in S_0. In $(CH_3)_2CS$, the strongest progression is observed to attach to the system origin in intervals of -153.2 and -144.5 cm^{-1}. The corresponding pattern in the spectrum of $(CD_3)_2CS$, -114.7, -108.8, and -105.0 cm^{-1} allows the intervals to be identified. The isotope ratios of the first intervals in $(CH_3)_2CS/(CD_3)_2CS$ of 153.2/114.7 cm^{-1} lead to the assignment to methyl torsion, T_1^0. Here the bands are labeled by the usual notation with the torsion
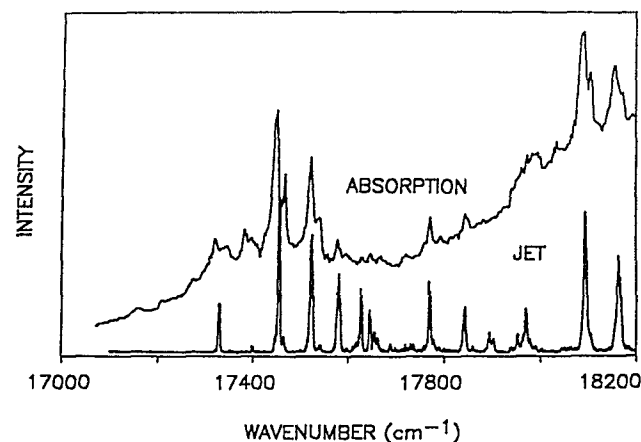

FIG. 1. The visible spectrum of thioacetone $(CH_3)_2CS$. The upper tracing is a digitized microdensitometer record of the photographically recorded long path length absorption spectrum. The lower tracing is the supersonic jet laser excitation spectrum.

TABLE I. Observed band heads in the excitation spectrum of $(CH_3)_2CS$.[a]

Observed	Difference	Assignment[b]	Observed	Difference	Assignment
17 030.1	− 297.7	T_2^0	17 894.7	+ 566.9	$B_0^1 T_0^2$
17 082.6	− 245.2		17 970.3	+ 642.5	S_0^1
17 174.6	− 153.2	T_1^0	18 092.9	+ 765.1	$S_0^1 T_0^1$
17 220.5	− 107.3		18 162.7	+ 834.9	$S_0^1 W_0^1$
17 283.8	− 44.0		18 218.9	+ 891.1	$S_0^1 T_0^2$
17 327.8	0.0	0_0^0	18 266.9	+ 939.1	
17 399.6	+ 71.8		18 292.0	+ 964.2	
17 454.8	+ 127.0	T_0^1	18 352.0	+ 1024.2	
17 522.8	+ 195.0	W_0^1	18 368.6	+ 1040.8	
17 580.5	+ 252.7	T_0^2	18 407.7	+ 1079.9	$S_0^1 B_0^1 T_0^1$
17 627.8	+ 300.0	$T_0^1 W_0^2$	18 479.5	+ 1151.7	$S_0^1 B_0^1 W_0^1$
17 646.1	+ 318.3	B_0^1	18 688.6	+ 1360.8	
17 655.2	+ 327.4	T_0^3	18 728.7	+ 1400.9	$S_0^2 T_0^1$
17 769.1	+ 441.3	$B_0^1 T_0^1$	18 797.7	+ 1469.9	$S_0^2 W_0^1$
17 843.7	+ 515.9	$B_0^1 W_0^1$			

[a] In cm^{-1}.
[b] T (torsional mode), W (wagging mode), B (CCC bending mode), S (C—S stretching mode).

mode designated T and the wagging mode W.

Harmonic vibrational frequencies were calculated for thioacetone by *ab initio* theory at the 3-21G* level and are given in Table III. Under the C_{2v} symmetry operations of the rigid molecule, thioacetone has two normal modes which correspond to internal rotation: the clockwise–clockwise a_2 rotation of the methyl groups and the clockwise–counterclockwise b_1 rotation. For the $\nu_{12}(a_2)$ torsional mode in $(CH_3)_2CS/(CD_3)_2CS$ the calculated harmonic frequencies were found to be 93.95/66.61 and for $\nu_{17}(b_1)$, 147.70/107.57 cm^{-1}. These calculations allow the observed mode T to be assigned to the normal coordinate Q_{17}. The formation of progressions in the antisymmetric b_1 mode immediately leads to the conclusion that the conformation of the methyl groups in the T_1 state differs from that of the S_0

ground state and that the excitation process involves a structural distortion in the b_1 out-of-plane direction.

The assignment of the low temperature supersonic jet spectra of Fig. 4 that lies to the blue of the system origin was aided by molecular orbital calculations. The Hartree–Fock UHF/6-31G* scheme was employed for the T_1 state and four molecular structures were investigated. In the first set of calculations, the sulphur atom was fixed in the planar position ($\alpha = 0.0°$) and the methyl groups oriented in the (e,e) and (a,a) conformations. The energy difference between these two structures was found to be small, 37.99 cm^{-1}, with the (a,a) form being the more stable. That is, for the case of the planar frame, the two methyl groups undergo a 60° rotation on excitation from the (e,e) conformation of the S_0 state to an (a,a) conformation in the T_1 state. With

TABLE II. Observed band heads in the excitation spectrum of $(CD_3)_2CS$.[a]

Observed	Difference	Assignment[b]	Observed	Difference	Assignment
16 978.9	− 370.9		17 868.7	+ 518.9	$B_0^1 W_0^1 T_0^1$
17 021.3	− 328.5	T_3^0	17 891.5	+ 541.7	$B_0^1 T_0^3$
17 126.3	− 223.5	T_2^0	17 944.8	+ 595.0	S_0^1
17 133.9	− 215.9		18 044.4	+ 694.6	$S_0^1 T_0^1$
17 235.1	− 114.7	T_1^0	18 114.0	+ 764.2	$S_0^1 W_0^1$
17 278.0	− 71.8		18 139.5	+ 789.7	$S_0^1 T_0^2$
17 349.8	0.0	0_0^0	18 185.8	+ 836.0	$S_0^1 T_0^1 W_0^1$
17 451.2	+ 101.4	T_0^1	18 212.9	+ 863.1	$S_0^1 T_0^3$
17 523.6	+ 173.8	W_0^1	18 257.6	+ 907.8	
17 547.9	+ 198.1	T_0^2	18 273.0	+ 923.2	
17 593.2	+ 243.4	$T_0^2 W_0^1$	18 284.2	+ 934.4	
17 620.4	+ 270.6	T_0^3	18 316.5	+ 966.7	$S_0^1 B_0^1 T_0^1$
17 680.6	+ 330.8		18 352.0	+ 1002.2	
17 692.5	+ 342.7		18 386.7	+ 1036.9	$S_0^2 B_0^1 W_0^1$
17 724.0	+ 374.4	$B_0^1 T_0^1$	18 410.6	+ 1060.8	
17 795.5	+ 445.7	$B_0^1 W_0^1$	18 460.6	+ 1110.8	
17 818.0	+ 468.2	$B_0^1 T_0^2$			

[a] In cm^{-1}.
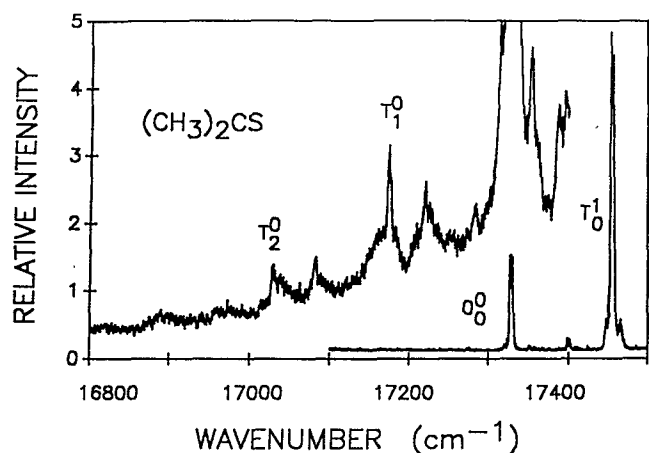[b] T (torsional mode), W (wagging mode), B (CCC bending mode), S (C—S stretching mode).

FIG. 2. A comparison of the supersonic jet excitation spectra of $(CH_3)_2CS$ with the excitation spectrum recorded under conditions which accentuate the hot band structure.
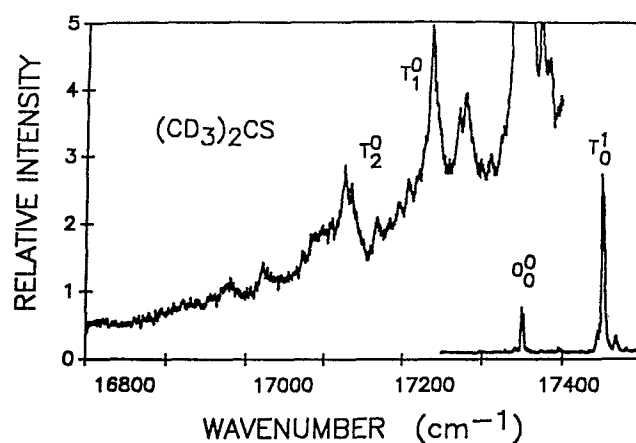

FIG. 3. A comparison of the laser excitation spectra of $(CD_3)_2CS$ recorded in a warm jet and under supersonic jet temperatures.

full optimization of all coordinates, it was found that the sulphur adopts a nonplanar equilibrium structure with $\alpha = 27.36°$. This result is not too surprising as molecules which bear the carbonyl or thiocarbonyl chromophore are known to undergo pyramidal distortions as a result of $n \to \pi^*$ electron promotion.[14] The interesting feature of this calculation, however, is that in the equilibrium configuration of the

T_1 state, the methyl groups are found to be rotated by 10.93° from the (e,e) conformation in a counterclockwise–clockwise direction in such a way as to preserve the symmetry plane which bisects the molecule. The barrier height to internal rotation in the nonplanar equilibrium configuration was established in the final calculation. In this case, the out-of-plane angle was fixed at $\alpha = 27.36°$ and the torsional angles rotated by 60.0° to give a barrier of 1240.64 cm^{-1}. The re-

TABLE III. Calculated[a] vibrational frequencies for the S_0 and T_1 states of thioacetone.[b]

		S_0	State			T_1	State
	C_{2V}	$(CH_3)_2CS$	$(CD_3)_2CS$			$(CH_3)_2CS$	$(CD_3)_2CS$
	ν_1	2952.47	2186.75		ν_1	2899.62	2148.29
	ν_2	2840.61	2041.76		ν_2	2871.92	2118.92
	ν_3	1475.54	1237.28		ν_3	2814.31	2024.42
a_1	ν_4	1402.63	1081.59		ν_4	1481.43	1100.84
	ν_5	1269.38	1047.36		ν_5	1479.54	1068.60
	ν_6	994.67	815.11		ν_6	1408.69	1061.84
	ν_7	651.08	602.65		ν_7	1180.20	1038.92
	ν_8	360.46	308.35		ν_8	1048.96	847.05
				a'	ν_9	846.22	734.16
	ν_9	2873.31	2124.71		ν_{10}	566.63	529.96
	ν_{10}	1458.30	1053.31		ν_{11}	318.74	274.54
a_2	ν_{11}	936.43	712.28		ν_{12}	234.24	210.81
	ν_{12}	93.95	66.61		ν_{13}	145.20	104.82
	ν_{13}	2881.71	2131.18		ν_{14}	2897.22	2145.22
	ν_{14}	1479.23	1064.26		ν_{15}	2870.04	2117.74
b_1	ν_{15}	1080.39	914.99		ν_{16}	2811.49	2022.34
	ν_{16}	433.87	370.74		ν_{17}	1467.66	1107.00
	ν_{17}	147.70	107.57	a''	ν_{18}	1466.63	1058.10
					ν_{19}	1393.66	1057.52
	ν_{18}	2951.12	2183.59		ν_{20}	1097.85	1006.27
	ν_{19}	2833.05	2036.11		ν_{21}	972.59	752.06
	ν_{20}	1451.09	1115.08		ν_{22}	949.41	731.11
b_2	ν_{21}	1386.50	1043.31		ν_{23}	273.18	250.23
	ν_{22}	1140.09	1011.87		ν_{24}	144.62	103.12
	ν_{23}	903.51	729.31				
	ν_{24}	374.30	341.14				

[a] Values in cm^{-1}, scaled by 0.89.
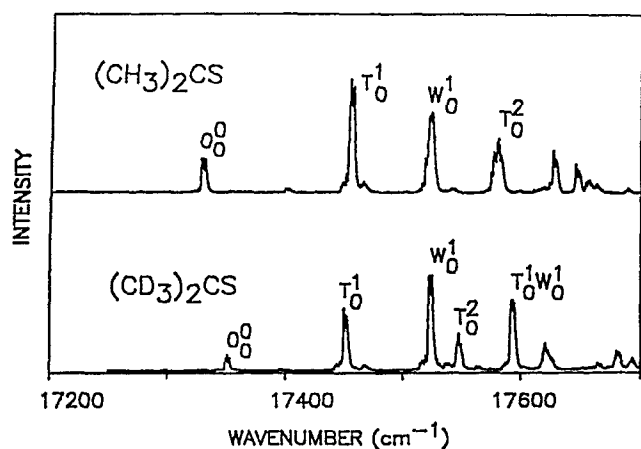[b] 3-21 G* basis, calculated at optimized geometry.

FIG. 4. The supersonic jet laser excitation spectra of thioacetone-*h* 6 and thioacetone-*d* 6.

sults, which are collected together in Table IV, show that the barrier for methyl rotation is dependent on pyramidalization. When the frame is planar, ($\alpha = 0.0°$), the barrier is low, 37.99 cm^{-1}, and the conformation is (a,a) ($\Theta_1 = \Theta_2 = 60°$). In the equilibrium configuration ($\alpha = 27.36°$, $\Theta_1 = \Theta_2 = 10.93°$) the barrier is relatively high, 1240.63 cm^{-1}, and the internal rotation is reduced to restricted torsional oscillation.

It is possible to make a prediction of the mode activity from the structural calculations of Table IV. The equilibrium values of the r(C=S) bond for the S_0/T_1 states were calculated to be 1.6169/1.7583 Å, respectively. The increase in bond length of 0.1414 Å is greater than would be expected[14] for a reduction in C=S bond order from 2 to 1.5. It should, however, create an extensive progression in the thiocarbonyl stretching mode. The vibrational frequencies cal-

culated for the T_1 state with the 3-21G* basis place ν_{10}(C=S) for $(CH_3)_2CS/(CD_3)_2CS$ at 566.63/529.96 cm^{-1}. The corresponding intervals are found in the spectrum at + 642.5/ + 595.0 cm^{-1}. Table IV also shows that the CCC angle increases from 114.45° to 119.16° on excitation. The ν_{12} mode, which most closely corresponds to CCC bending, is calculated to be 318.74/274.54 cm^{-1} for the two isotopomers. The intervals of + 318.3/ + 272.8 cm^{-1} are given this assignment.

The final assignment concerns the large amplitude sulphur wagging and methyl rotation modes. With the pyramidal distortion of the sulphur atom and the rotation of the methyl groups, the rigid symmetry of the upper T_1 state falls from C_{2v} to C_s. As a result, the vibrational modes in the upper state can be classified as symmetric, a', or antisymmetric, a'', with respect to the vertical plane. The ν_{17} (b_1) methyl torsion and ν_{16} (b_1) wagging modes are of a' symmetry in the rigid pyramidal upper state. Both of these modes would be active in a singlet triplet transition as a result of the $a' \leftrightarrow a'$ and $a'' \leftrightarrow a''$ selection rules. The calculated values in the harmonic approximation are ν_{12} (a') = 234.24/210.81 cm^{-1} for the wagging mode and ν_{13} (a') = 145.20/104.82 cm^{-1} for the torsional mode. The first intervals observed in the low temperature supersonic jet spectra of $(CH_3)_2CS/(CD_3)_2CS$ terminate in strong bands at + 127.0/101.4 cm^{-1}. These bands can be grouped together to form a progression of 3–4 members. From the above calculations, the assignment is made to the activity of methyl torsion ν_{13} (a'). A second progression can be identified which attaches to the origin in intervals of + 195.0/ + 173.8 cm^{-1}. From the calculated values, 234.24/210.81 cm^{-1}, the assignment to the sulphur wagging mode, ν_{12} (a') follows. The activity of the sulphur wagging mode is to be anticipated since thiocarbonyl molecules in the S_0 or T_1 states are nonplanar at the sulphur center. Thus the

TABLE IV. Calculated energies and structural parameters for S_0 and T_1 thioacetone with different conformations of the methyl group.

Θ_1	Θ_2	α	Energy[a]	Difference[b]	r(C=S)[c]	r(CC)[e]	α(CCC)[d]
			S_0 electronic state				
0.00	0.00	0.00	− 514.593 987 8	0.00	1.6169	1.5063	114.45
30.00	0.00	0.00	− 514.593 129 0	188.48	1.6177	1.5048	114.88
						1.5089	
30.00	30.00	0.00	− 514.592 324 2	365.13	1.6184	1.5074	115.30
60.00	0.00	0.00	− 514.592 220 4	387.91	1.6182	1.5034	115.31
						1.5121	
30.00	− 30.00	0.00	− 514.591 179 0	616.47	1.6194	1.5098	116.24
60.00	60.00	0.00	− 514.588 939 9	1107.88	1.6205	1.5121	117.50
60.00	30.00	0.00	− 514.590 560 1	752.28	1.6194	1.5121	116.49
						1.5076	
			T_1 electronic state				
0.00	0.00	0.00	− 514.549 837 7	0.00	1.7492	1.5027	120.57
60.00	60.00	0.00	− 514.550 010 8	− 37.99	1.7539	1.5032	124.52
10.93	− 10.93	− 27.36	− 514.552 304 8	− 541.46	1.7583	1.5048	119.16
79.03	− 79.03	− 27.36	− 514.546 652 0	699.17	1.7613	1.5130	121.22

[a] In a.u.
[b] In cm^{-1}.
[c] In angstroms.
[d] In degrees.
[e] C_1 symmetry unequal CC bond lengths.

modes Q_{12}, Q_{13}, and Q_{24} would be of large amplitude and would describe the low frequency dynamics of the T_1 state.

DISCUSSION

In the lower S_0 electronic state,[8,9] thioacetone has a C_{2v} equilibrium structure and the in-plane methyl hydrogens eclipse the sulphur atom. The methyl groups, however, are flexible and oscillate about the carbon–carbon single bonds. As the barriers to hindered internal rotation are relatively low, the torsional potential is governed by cosine-type functions with the result that the energy levels split into torsional sublevels. To obtain a further insight into the dynamics of the ground state we performed calculations with a coupled two oscillator model.

The Hamiltonian operator for a system bearing two equivalent C_3 rotors attached to a C_{2v} rigid molecular frame can be written,[15-18] in the C_3 symmetric and rigid rotor approximation as

$$\hat{H}(\theta_1,\theta_2) = -B_{11}\frac{\partial^2}{\partial\theta_1^2} - 2B_{12}\frac{\partial^2}{\partial\theta_1\partial\theta_2}$$
$$-B_{22}\frac{\partial^2}{\partial\theta_2^2} + V(\theta_1,\theta_2),\tag{1}$$

where B_{11} and B_{22} are the internal rotation constants for the methyl groups and B_{12} is the kinetic interaction term. The torsional angles θ_1 and θ_2 for this system are defined by the coordinates of Fig. 5.

The rotational constants are related to the reduced moments of inertia by the following expressions:

$$B_{11} = \frac{\hbar^2}{2}\frac{I_1}{I_1^2 - \Lambda_{12}^2},\tag{2}$$

$$B_{12} = \frac{\hbar^2}{2}\frac{\Lambda_{12}}{I_1I_2 - \Lambda_{12}^2}.\tag{3}$$

In these expressions I_1 and I_2 are the reduced moments of inertia of the rotors and Λ_{12} is the interaction term.

$$\Lambda_{12} = \sum_{i=xyz} A_1A_2\lambda_{1i}\lambda_{2i}/M_{ii},\tag{4}$$

$$I_1 = A_1\left(1 - \sum_{i=xyz} A_1\lambda_{1i}^2/M_{ii}\right),\tag{5}$$

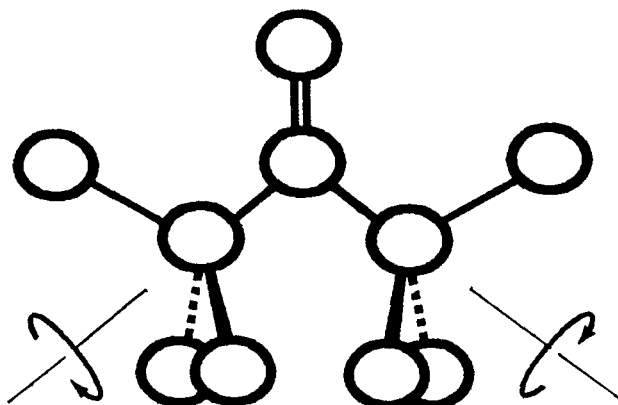FIG. 5. The torsional coordinates for thioacetone.

where A_1 and A_2 are the moments of inertia of the two CH_3 groups, λ_{1i} and λ_{2i} are the direction cosines between the axes of the methyl group, and the ith principal axis with moment M_{ii}.

The existence of the symmetry planes in the CH_3 rotors and in the frame of the molecule allows the nonrigid group of the complete set of the symmetry operations which commute with the Hamiltonian operator Eq. (1) to be expressed as

$$G_{NRG} = (C_3^{I1}\times C_3^{I2}) \wedge (V^I \times W^I) \sim G_{36}\tag{6}$$

which is a group of order 36 and is isomorphic to the Longuet–Higgins molecular symmetry group,[18,19] G_{36}. The caret means semidirect product. In this expression, the C_3^{I1} and the C_3^{I2} are the threefold rotation subgroups of each rotor. V^I and W^I are, respectively, the double switch and exchange subgroups defined as follows:

$$C_3^I = [\hat{E} + \hat{C}_3 + \hat{C}_3^2],\tag{7}$$

$$V^I = [\hat{E} + \hat{V}],\tag{8}$$

$$W^I = [\hat{E} + \hat{W}],\tag{9}$$

where $\hat{C}_3$, $\hat{V}$, and $\hat{W}$ are the rotation, double switch, and exchange operators, respectively,

$$\hat{V}f(\theta_1,\theta_2) = f(-\theta_1,-\theta_2),\tag{10}$$

$$\hat{W}f(\theta_1,\theta_2) = f(\theta_2,\theta_1).\tag{11}$$

The potential function for internal rotation in planar thioacetone can be developed in terms of the A_1 symmetry eigenvectors:

$$V(\theta_1,\theta_2) = \sum_K\sum_L A_{KL}^{CC}(\cos 3K\theta_1 \cos 3L\theta_2$$
$$+\cos 3L\theta_1 \cos 3K\theta_2)$$
$$+A_{KL}^{SS}(\sin 3K\theta_1 \sin 3L\theta_2$$
$$+\sin 3L\theta_1 \sin 3K\theta_2).\tag{12}$$

The Schrödinger equation for the two coupled rotor problem, Eq. (1) were solved variationally. The solutions were expanded in terms of a set of the free rotor basis functions:

$$\Phi = \sum_I\sum_J (C_{IJ}^{CC}\cos I\theta_1 \cos J\theta_2$$
$$+C_{IJ}^{CS}\cos I\theta_1 \sin J\theta_2$$
$$+C_{IJ}^{SC}\sin I\theta_1 \cos J\theta_2 + C_{IJ}^{SS}\sin I\theta_1 \sin J\theta_2)$$
$$\tag{13}$$

and the expansion coefficients were determined variationally.

The terms in the potential energy function Eq. (12) were determined from *ab initio* molecular calculations by means of the GAMESS program.[20] A 6-31G* basis set was employed for the molecular orbital (MO) calculations and the restricted Hartree–Fock (RHF) and UHF schemes were used for the S_0 ground and T_1 excited states. The molecular structures for selected values of the torsional angles θ_1,θ_2 were fully optimized. Structural parameters for the eclipsed–eclipsed (e,e) $(\theta_1 = \theta_2 = 0.0°)$ and antieclipsed–antieclipsed (a,a) $(\theta_1 = \theta_2 = 60.0°)$ conformations of the

TABLE V. Molecular structures[a] of S_0 thioacetone for the eclipsed–eclipsed $(0°,0°)$ and antieclipsed–antieclipsed $(60°,60°)$ conformations.[b]

Parameter	$(0°,0°)$	$(60°,60°)$	Parameter	$(0°,0°)$	$(60°,60°)$
$r(C{=}S)$	1.6169	1.6209	$\alpha(CCH_a)$	111.65	112.52
$r(CC)$	1.5064	1.5123	$\alpha(CCH_b)$	109.69	109.62
$r(CH_a)^c$	1.0791	1.0841	$\alpha(H_aCH_b)$	121.37	121.33
$r(CH_b)^d$	1.0873	1.0837	$\alpha(H_bCH_b)$	117.26	117.34
$\alpha(CCC)$	114.45	117.54			

[a] Fully optimized structures with 6-31G* basis.
[b] Parameters in angstroms and degrees.
[c] CH_a in-plane carbon–hydrogen bond.
[d] CH_b out-of-plane carbon–hydrogen bonds.

TABLE VI. Calculated expansion coefficients and the reduced internal rotation constants for S_0 thioacetone.[a]

Coefficient	Value	Coefficient	Value
A^{CC}_{00}	475.622	A^{CC}_{21}	2.464
A^{CC}_{10}	−279.434	A^{CC}_{22}	5.238
A^{CC}_{11}	83.015	A^{SS}_{11}	−125.670
A^{CC}_{20}	−4.968		
Int. rot. const.		$(CH_3)_2CS$	$(CD_3)_2CS$
$B_{11} = B_{22}$		5.657 19	2.899 19
B_{12}		−0.048 00	−0.053 70

[a] Values in cm^{-1}.

ground state are given in Table V. As would be expected, the structural coordinates are sensitive to the conformation of the methyl groups.

In particular, the $\alpha(CCC)$ angle in the (e,e) structure was calculated to be 114.45° and to increase to 117.54° as the methyl groups rotate by 60° to the (a,a) conformation. The change in the $r(C{=}S)$ bond length is less dramatic, increasing from 1.6169 to 1.6205 Å with methyl rotation. The struc-

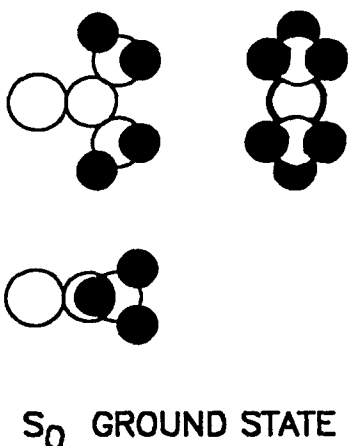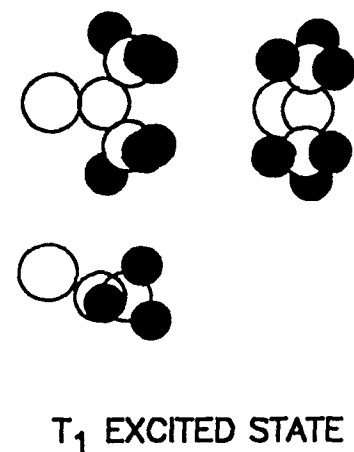tures of (e,e) thioacetone in both electronic states are illustrated in Fig. 6.

Table IV collects the energy data points for the potential surfaces as a function of torsional angles. With the energy of the (e,e) conformation in S_0 scaled to 0.0 cm^{-1}, the energy of the potential maximum (a,a) is 1107.88 cm^{-1} and that of the saddle point, (e,a) is 387.91 cm^{-1}. These results compare favorably with those of Fausto et al.[21] who used a 4-31 basis and calculated the (e,a) saddle point to be 384 cm^{-1}. Table VI gives the reduced internal rotation constants for S_0 $(CH_3)_2CS$ and $(CD_3)_2CS$, along with the Fourier coefficients for the potential Eq. (12) which were obtained from fitting the data points of Table IV.

Figure 7 shows a 120°×120° segment of the ground state potential surface. For a full 360° rotation of the methyl groups this "egg box" potential contains 9 minima. It is clear that the walls of the potential are steeper in the direction where the methyl groups rotate in opposite senses, b_1 in the rigid C_{2v} notation, than they are in the direction where the rotors move in the same direction, a_2. Thus it would be anticipated that the b_1 torsional mode would be of higher frequency than the a_2 mode.

T_1 EXCITED STATE

S_0 GROUND STATE

FIG. 6. The calculated molecular structures of thioacetone in the S_0 and T_1 electronic states (top, end, and side views).

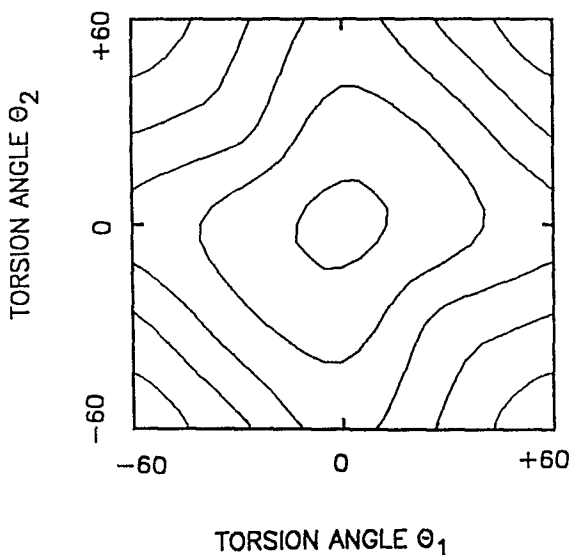FIG. 7. One segment of the egg box potential surface for methyl internal rotation in thioacetone. Each contour represents 200 cm^{-1}.

TORSION ANGLE Θ_2

TORSION ANGLE Θ_1

TABLE VII. Torsional energy levels for the S_0 state of thioacetone calculated[a] from *ab initio* potential constants.[b]

				$(CH_3)_2CS$				
A_1	A_2	A_3	A_4	G	E_1	E_2	E_3	E_4
131.38	291.35	232.52	366.60	131.55	131.72	233.90	131.72	291.78
347.57	478.57	469.41	519.87	233.35	291.79	376.18	233.91	376.20
435.55	584.15	515.63	640.70	291.34	353.29	457.00	353.27	460.94
526.21	690.03	680.37	777.35	350.04	443.88	510.19	443.50	572.07
616.05	780.03	760.02	836.31	371.63	463.76	599.36	460.17	611.60
				$(CD_3)_2CS$				
A_1	A_2	A_3	A_4	G	E_1	E_2	E_3	E_4
94.032	212.97	165.78	275.92	94.592	95.162	170.20	95.160	217.46
250.78	355.86	340.65	424.68	168.09	217.49	288.72	170.21	288.71
328.73	445.30	386.28	486.30	214.94	260.74	359.06	260.79	374.44
423.54	534.35	529.56	560.84	255.25	341.67	404.06	341.57	459.64
456.40	575.49	561.76	664.75	282.52	374.43	471.09	359.22	473.33

[a] From the parameters of Table III.
[b] In cm^{-1}.

The Schrödinger equation corresponding to the Hamiltonian operator (1) was solved variationally by expanding the solutions in terms of the symmetry eigenvectors. Each methyl rotor was described by 31 basis functions to give an overall order of 961 for the Hamiltonian matrix. This was factorized into 16 blocks, corresponding to the representations of the G_{36} group: A_1 (36), A_2 (30), A_3 (30), A_4 (25), G (4×110), E_1 (2×55), E_2 (2×45), E_3 (2×55), and E_4 (2×45). The first five torsional levels of each representation for the two isotopomers of S_0 thioacetone are given in Table VII. As the potential surface has nine minima for every complete rotation of the methyl group, the zero point level has nine microstates. From Table VII these can be identified as belonging to the A_1, E_1, E_3, and G representations.

The selection rules for a transition between a singlet and a triplet electronic state in the nonrigid approximation are $A_1 \leftrightarrow A_1$, $A_2 \leftrightarrow A_2$, $A_3 \leftrightarrow A_3$, $A_4 \leftrightarrow A_4$, $G \leftrightarrow G$, $E_1 \leftrightarrow E_1$, $E_2 \leftrightarrow E_2$, $E_3 \leftrightarrow E_3$, $E_4 \leftrightarrow E_4$. Table VII shows that the zero point level contains four microlevels: A_1, E_1, E_3, and G. Thus, it is the transitions $A_1 \leftrightarrow A_1$, $E_1 \leftrightarrow E_1$, $E_3 \leftrightarrow E_3$, and $G \leftrightarrow G$ which could provide the intensity for the origin band. The calculated frequencies of Table VII show, however, that it is the pairs of levels connected by the $A_1 \leftrightarrow A_2$, $A_2 \leftrightarrow A_1$, $E_1 \leftrightarrow E_1$, and $G \leftrightarrow G$ transitions which could be responsible for the $+ 127.0/ + 101.4$ cm^{-1} intervals. The symmetry properties of a flexible pyramidal upper electronic state[16] give rise to a nonrigid group which is found to be isomorphic to the G_{36} rigid planar frame group of the lower state. The major difference between these two groups is that the $A_1 + A_2$ representations of the planar case correlates to a mixed A_1 representation when the frame is pyramidal. Thus, the singly degenerate wave functions for the T_1 state, $\Psi_{A1} \cdots \Psi_{A4}$ can be written in terms of the $\psi_{A1} \cdots \psi_{A4}$ functions of the S_0 state as

$$\Psi_{A1} = A\psi_{A1} \cos M\alpha + B\psi_{A2} \sin M\alpha,$$
$$\Psi_{A2} = B\psi_{A1} \sin M\alpha - A\psi_{A2} \cos M\alpha,$$

$$\Psi_{A3} = C\psi_{A3} \cos M\alpha + D\psi_{A4} \sin M\alpha, \qquad (14)$$
$$\Psi_{A4} = D\psi_{A3} \sin M\alpha - C\psi_{A4} \cos M\alpha,$$

where $\cos M\alpha$ and its component $\sin M\alpha$ are wave functions for the flexible sulphur wagging coordinate. The angle α defines the out-of-plane displacement of the C=S bond. From the expression for Ψ_{A1} it is clear that when the upper T_1 state is planar ($\alpha = 0.0°$), $\Psi_{A1} = A\psi_{A1}$, whereas when the C=S bond swings perpendicular to the plane ($\alpha = 90.0°$), then $\Psi_{A1} = B\psi_{A2}$. Thus the assignment of the electronic transition to an $A_1 \leftrightarrow A_2$ combination is a result of the mixing of the A_1 and A_2 representations in the T_1 upper electronic state which is brought about by the nonplanar distortions of the frame.

The potential surface illustrated in Fig. 7 is a $- 60°$ to $+ 60°$ segment of the egg box potential which, for a complete rotation of the methyl groups, contains nine minima. In the region of the equilibrium position, the contour lines of isoenergy are oblong rather than circularly shaped as a result of the large $A_{11}^{SS} = - 125.670$ cm^{-1} coupling term. In the case of the b_1 torsion, the normal coordinate tracks in the $\Theta_1 = \Theta_2$ direction which rises at a 45° diagonal from the equilibrium position. The energy at $\Theta_1 = + 30°$, $\Theta_2 = + 30°$ of 616.47 cm^{-1} is to be compared to the value for $\Theta_1 = + 30°$, $\Theta_2 = - 30°$ of 365.13 cm^{-1} which is the equivalent point for torsional motion in the a_2 direction. Both of these one-dimensional slices out of the energy surface have identical barrier heights at $\Theta_1 = \Theta_2 = 60°$ of 1107.88 cm^{-1}. Thus, the potential for torsion along the b_1 diagonal is narrow with steep walls and can be described as V-shaped while the potential along a_2 is U-shaped with a flat bottom. The fundamental and their first overtone frequencies of the torsional modes are a reflection of these one-dimensional potentials. For the $(CH_3)_2CS$ b_1 mode, the calculated level separations display positive anharmonicity, $159.97/144.20$ cm^{-1}, while for the a_2 mode the anharmonicity is reversed, $101.14/115.05$ cm^{-1}.

TABLE VIII. Observed and calculated vibrational frequencies for S_0 and T_1 thioacetone.[a]

| | | $(CH_3)_2CS$ | | $(CD_3)_2CS$ | |
		Observed	Calculated	Observed	Calculated
$T_1(b_1)$	ν_{17} (tor.)	153.2	159.97[c]	114.7	118.94[c]
			147.70[d]		107.57[d]
$T_2(b_1)$	$2\nu_{17}$ (tor.)	297.7	304.17[c]	223.5	234.70[c]
$T^1(a')$	ν_{13} (tor.)	127.0	145.20[d]	101.4	104.82[d]
$T^2(a')$	$2\nu_{13}$ (tor.)	252.7		198.1	
$W^1(a')$	ν_{12} (wag.)	195.0	234.24[d]	173.8	210.81[d]
$B^1(a')$	ν_{11} (CCC)	318.3	318.74[d]	273.0[b]	274.54[d]
$S^1(a')$	ν_{10} (C = S)	642.5	566.63[d]	595.0	529.96[d]
0_0^0	Elect. origin	17 327.8		17 349.8	

[a] Values in cm^{-1}.
[b] From $B_0^1 T_0^1 - T_0^1$.
[c] Two-dimensional approximation.
[d] Harmonic approximation.

In our earlier study,[11] the potential surface for the ground state was mapped out with the basis: 4-31 $+ d$ on sulphur. In that calculation, the CCC angle was fixed at 117.73° for the seven conformations which are needed to determine the potential surface. This 117.73° angle, corresponds to the 117.50° angle obtained here for the fully relaxed (a,a) structure. As a result, the potential in the earlier work was calculated to be too flat and too smooth at the (e,e) equilibrium position. As the selection rules only allow for the combination of identical representations in the two electronic states, the assignment was made to $A_1 \leftrightarrow A_1$. The recent symmetry considerations[15] for a flexible pyramidal triplet state allow for the mixing of the A_1 and A_2 representations and for the $A_1 \leftrightarrow A_2$ combination used here.

Additional MO calculations were carried out on the S_0 state with extended basis sets, 6-31G**, and with corrections for electron correlation, 6-31G* (MP2), at the 6-31G* geometry of Table II. For the sake of comparison, the $V(0°, 60°)$ position for the group of calculations 6-31G*/6-31G**/6-31G* (MP2) yielded the energies 387.89/388.18/447.97 cm^{-1} and for $V(60°, 60°)$, 1107.87/1112.00/1197.42 cm^{-1}. These results indicate that the inclusion of p-type orbitals on the hydrogen with the 6-31G** basis does not greatly alter the energy, whereas the correction for electron correlation has the effect of increasing the barrier height by 89.55 cm^{-1}. As the calculated frequencies are already higher than the observed values, the correction for electron correlation will not improve the fit to the experimental data. The calculated potential energies are higher than they are in the corresponding carbonyl compound, acetone. For $(CH_3)_2CO/(CH_3)_2CS$ the energy points are $V(60°, 0°)$ 246.85/387.91 and $V(60°, 60°)$ 763.92/1107.88 cm^{-1}, respectively. Since the CCC angles in the (e,e) conformation are very similar, 116.70°/116.49°, the differences in energy must come from the greater polarizability of the sulphur atom relative to that of oxygen. In the case of acetone,[22,23] the b_1 fundamental and the first overtone intervals have been measured to be 125.16/102.92 cm^{-1}, and for the a_2 mode: 77/89 cm^{-1}. The most recent *ab*

initio MO calculations[24,25] place these frequencies at 130.41/104.26 and 79.54/84.31 cm^{-1}, respectively. As in the case of thioacetone, the calculated fundamental frequencies are higher than the observed frequencies and neither improvements in the basis set nor corrections for electron correlation appear to improve the fit. The source for the discrepancy undoubtedly arises from a coupling of the torsional modes with the low frequency CCC bending mode.

The observed spectroscopic data are summarized in Table VIII. The T_1 ν_{10} (C=S) fundamental for the two isotopomers is observed at 642.3/595.0 cm^{-1} which is somewhat higher than the calculated frequencies, 566.63/595.0 cm^{-1}. The values are lower than those of the simple thioacarbonyl compounds:[14] H_2CS (859); Cl_2CS (923); Br_2CS (895); CH_3CHS (742) cm^{-1}. The weak bands at 318.3/272.8 cm^{-1} are assigned to the ν_{11} (CCC) bending mode on the basis of the calculated frequencies 318.7/274.2 cm^{-1}. The activity of this mode is a result of the calculated $+4.71°$ increase in the CCC angle which occurs on excitation to the T_1 state.

The activity of the ν_{23} (wagging) mode is a consequence of the pyramidal distortion at the sulphur end of the molecule. The *ab initio* calculations show that the C=S bond is directed out of the CCC plane by 27.36°. As a result of the coupling between the wagging and the torsional coordinates, the potential governing the low frequency motions is complex. For example, the calculations of Table IV show that when the frame of the molecule is held in the planar configuration, $\alpha = 0.0°$, the T_1 state adopts the (a,a) conformation with a barrier to internal rotation of 37.99 cm^{-1}. That is, there is a 60° rotation of the methyl groups on singlet–triplet excitation. Similar conformational changes have been observed in methyl groups which are directly bonded to the N=O, C=O, and C=S chromophores.[6,26] The phenomena, which appear to be wide spread, have been attributed to the differences in hyperconjugation in the p-type methyl group orbitals and the π bond of the thiocarbonyl group. In the lower S_0 state, the π-type interaction between the sulphur and hydrogen atoms is repulsive and the (e,e) confor-

mation is favored, whereas, in the upper T_1 state the hyperconjugative effects are attractive and the (a,a) conformation is stabilized. The low barrier to internal rotation in the planar T_1 configuration presumably is a consequence of a balancing of the opposing effects of steric repulsion and hyperconjugation.

The T_1 frequencies calculated in the harmonic approximation for the large amplitude modes: ν_{13} (a' torsion) $= 145.20 \text{ cm}^{-1}$ and ν_{12} (a' wagging) $= 234.24 \text{ cm}^{-1}$ do not give good agreement with the observed values, 153.2 and 195.0 cm^{-1}. This result is not surprising and may be directly attributed to the complex nature of the three-dimensional potential.

CONCLUSIONS

The excellent agreement between the calculated energy levels and the observed intervals in the hot band spectra demonstrates that the 6-31G* basis is capable of yielding a good quality potential surface for the ground electronic state. In the special case where structural conformation differs in the two electronic states connected by the electronic transition, the observed progressions in the torsional mode may go to quite high quantum numbers. As a result, information may be available from electronic excitation spectra which is not readily accessible from far-infrared absorption studies. Thus, additional experimental data could be obtained about the higher levels in the b_1 torsional manifold in thioacetone from resolved high resolution phosphorescence spectra recorded under supersonic jet conditions. Also, an ultraviolet two photon resonant multiphoton ionization study on the hot band structure in the Rydberg spectra of thioacetone, similar to that carried out for acetone,[23] would be useful in characterizing the a_2 torsional manifold.

Our understanding of the T_1 conformational properties of the upper state is less complete. The present study shows that the potential surface which describes internal rotation of the methyl groups is highly sensitive to nonplanarity at the sulphur center. For the case of a planar frame, the potential surface is relatively flat and the a,a conformation is the stable form. When the thiocarbonyl bond is tilted into its equilibrium configuration, the calculated barrier for internal rotation is high and the methyl groups rotate by only 10.93° from the e,e position. It follows that the flexibility problem of the upper state requires the solution to a large amplitude Hamiltonian which is dependent on both the methyl torsion and the sulphur wagging coordinates. The solution to this problem would provide information about the equilibrium structures and dynamics of the upper electronic state in a form which could be directly related to the observed spectra.

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