

VIBRATIONAL SPECTRA AND NORMAL COORDINATE ANALYSIS OF METHYL THIONITRITE AND ISOTOPIC ANALOGS

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ABSTRACT

The observed gas-phase IR frequencies for forty-four fundamentals of methyl thionitrite (CH_3SNO) and its d_3 -, ^{13}C -, and ^{15}N -substituted analogs have been used to calculate a nineteen-parameter symmetry valence force field. The final refinement resulted in an average error of less than 4 cm^{-1} ($\sim 0.5\%$) between the calculated and observed frequencies for the four isotopomers. Contrary to earlier reports, relative intensities, isotopic frequency shifts, as well as the calculated potential-energy distribution, all support the assignment of $\nu(\text{CS})$ to a higher frequency than that of $\nu(\text{SN})$. For the normal molecule, $\nu(\text{CS})$ is observed as a weak band at 735 cm^{-1} ; by contrast, $\nu(\text{SN})$ absorbs strongly at 646 cm^{-1} . The NO stretching fundamental occurs at 1535 cm^{-1} in the gas-phase spectrum of the unsubstituted molecule but shifts to 1507 cm^{-1} when ^{15}N replaces the normal isotope. The five fundamental bands associated with the skeletal vibrations of CH_3SNO are compared with the analogous absorptions in the spectra of CF_3SNO and CH_3ONO .

INTRODUCTION

Methyl thionitrite has been the subject of several spectroscopic investigations. Philippe studied the vapor-phase IR spectrum in the rock salt region, making the first tentative assignments of the fundamental frequencies [1]. He also made comparisons with the spectra of the other simple alkyl thionitrites [2] and later calculated a simple valence force field (SVFF) based on a simplified molecular model in which the methyl moiety was treated as if it were a hypothetical rigid group of atomic mass 15 [3].

Using grating instruments and a Michelson interferometer, Christensen et al. [4] extended the observed spectral range down to 50 cm^{-1} . In addition, they presented the first spectra of this volatile, unstable species in the liquid phase, both neat and in solution. About the same time, in an unpublished dissertation, Male [5] reported on the solid-state as well as gas-phase spectra for methyl thionitrite and its deuterated analog.

We carried out the present normal coordinate analysis to provide a comprehensive set of force constants to aid our current effort to interpret the spectra of more complex thionitrites of biologically important species, such as those of cysteine and glutathione, and to sort out certain inconsis-

tencies in the published assignments of the fundamental frequencies for CH_3SNO [1–5]. To accomplish this task, we synthesized four isotopic variants of methyl thionitrite, including the previously unreported ^{15}N - and ^{13}C -substituted species, and obtained gas-phase IR spectra. The calculated valence force field reported here includes values for 13 diagonal and six interaction constants. The two unobserved torsional modes are omitted.

EXPERIMENTAL

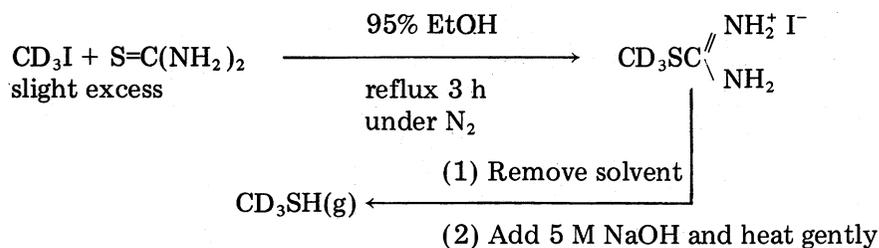
In contrast to earlier workers who synthesized methyl thionitrite by treating the pure thiol with N_2O_3 at low temperatures [1, 4, 5], we found it much more convenient to combine aqueous sodium nitrite with an acidic aqueous solution of the methanethiol. This procedure has three distinct advantages over earlier methods: first, the reaction, although quite fast, proceeds much more smoothly than that for the pure thiol with nitrogen trioxide; second, ^{15}N -enriched sodium nitrite is commercially available, facilitating the preparation of the methyl thionitrite containing this isotope; third, this reaction is virtually quantitative, leaving the thionitrite as the only volatile component at -78°C .

In more detail, the desired methanethiol isotopomer (~ 1.5 mmol) was transferred under high vacuum to a reaction tube containing ~ 20 ml 0.1 M HCl (aq). Just less than an equimolar quantity of NaNO_2 was dissolved in distilled H_2O (~ 20 ml). By means of Schlenk-type techniques [6], this solution was slowly added to the acidified solution of the thiol at ice-bath temperature. Then K_2HPO_4 (~ 0.38 g, ~ 2.2 mmol) dissolved in water (~ 5 ml) was added to the now pale red mixture to neutralize the HCl. Finally, the methyl thionitrite was distilled under high vacuum through a dry ice–ethanol trap (to collect water and any traces of the disulfide) and then into a liquid nitrogen trap. Methyl thionitrite is thermally unstable, particularly in the liquid phase. It decomposes only slowly, however, in the vapor phase, especially if shielded from low-energy UV radiation, such as emanates from fluorescent lamps. At -20°C and $P < 100$ torr, we have stored it relatively unchanged for more than a week.

Normal CH_3SH was from Matheson*; unlabelled sodium nitrite was Baker Analyzed, reagent grade; sodium nitrite- ^{15}N (95.7 atom %) was from Merck, Sharp, and Dohme, Canada, Ltd. Deuterated and ^{13}C -enriched methanethiol were synthesized from the respective methyl iodide analogs (99.5% D and 90% ^{13}C), both from Merck of Canada, according to the following scheme** [5, 7]

*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

**CAUTION: Thiourea, $\text{S}=\text{C}(\text{NH}_2)_2$, is reported in the Merck Index (8th edn.) to cause variable but acute toxicity in humans and should be handled with appropriate care. The product, methyl thionitrite, is of unknown toxicity, but like the parent thiol has a characteristic vile, nauseous odor and should be handled only in a well vented hood. The pure product should not be sealed in a small volume glass container as decomposition yields NO gas and thus potentially hazardous pressures.



The product was collected at -196°C on a vacuum line and purified by trap-to-trap distillation.

All IR spectra between $4000\text{--}250\text{ cm}^{-1}$ were obtained on a Perkin-Elmer 457 grating IR spectrophotometer. The instrument settings used were: scan speed = very slow; slit program = 3 (giving a nominal resolution of 2.1 cm^{-1} at 1000 cm^{-1}); and time constant = 2 s full scale. The 10-cm pathlength gas cell had CsI windows. Towards the conclusion of this study, supplementary spectra from $450\text{--}180\text{ cm}^{-1}$ were run on a Nicolet 7199 Fourier-transform IR spectrometer equipped with a $6.25\text{ }\mu\text{m}$ beamsplitter, a Globar source, and a TGS detector. Each spectrum was 128 scans at 4 cm^{-1} resolution and the interferogram was twice zero filled and transformed with the Happ-Genzel apodization function. The observed gas-phase IR frequencies and suggested vibrational assignments for the four methyl thionitrite isotopomers are collected in Table 1. Figures 1 and 2 show the four spectra.

COMPUTATIONS

Numerical methods and structural considerations

Numerical calculations for this vibrational analysis based on Wilson's GF-matrix formulation [8] were carried out by applying previously reported procedures and computer programs [9]. No structural studies are available for methyl thionitrite. Thus, the estimated molecular parameters chosen for determining the G matrix come from two sources: the value for the C—H bond length of the methyl group ($1.10\text{ }\text{\AA}$; $1\text{ }\text{\AA} = 100\text{ pm}$) is from microwave data for methanethiol vapor [10]; data for the —CSNO skeleton are from a single-crystal X-ray structure of the unusually stable thionitrite of *N*-acetyl-D,L-penicillimine [11]. The three pertinent bond lengths from the latter are C—S, $1.841\text{ }\text{\AA}$; S—N, $1.771\text{ }\text{\AA}$; and N—O, $1.214\text{ }\text{\AA}$. The two bond angles are CSN = 100.4° and SNO = 113.2° . The four bond angles around the carbon atom were idealized to tetrahedral geometry (109.47°). Finally, the molecule was assumed to be in an *anti* (or *trans*) conformation, so that the torsional angle CSNO equalled 180° . The basis for this structural assumption, as previously noted by Christensen et al. [4], is the observation of a distinct PQR structure for the band at $\sim 1300\text{ cm}^{-1}$ in the spectra of each of the three non-deuterated molecules. These bands are assigned to $\delta_s(\text{CH}_3)$. Only if the molecular conformation is *anti* (or nearly so) will the bond transition moment

TABLE 1

Observed IR frequencies (cm^{-1}) and assignments for methyl thionitrite and three isotopic derivatives

Assignment	CH_3SNO		CD_3SNO		$\text{CH}_3\text{S}^{15}\text{NO}$		$^{13}\text{CH}_3\text{SNO}$	
	ν^a	f^b	ν^a	f^b	ν^a	f^b	ν^a	f^b
$2\nu_3^c$	~3486 ~3100 sh { 3039 ~3028 sh }	~0.02 ~0.16 ~0.51	— ~3088 sh { 3036 3026 }	0.17 0.60	~3390 ~3043 sh { 2991 2976 }	~0.02 0.23 0.54	~3436 ~3100 sh { 3042 3029 }	~0.02 ~0.11 0.50
ν_2	(CH_3 str.)	0.47	—	—	2926	0.63	2926	0.50
$2\nu_4; 2\nu_{12}$	2830	0.14	—	—	~2829	0.17	2836	0.14
$\nu_1; \nu_{11}$	—	—	2246	0.08	—	—	—	—
$\nu_3 + \nu_8$	2184	0.06	—	—	~2136	0.04	2174	0.03
ν_2	{ R Q P }	—	2138 2128 ~2124	0.38	—	—	—	—
$\nu_3 + \nu_9$	{ R Q P }	0.43	1929 1924 ~1914 sh	0.60	1902 1891 ~1879 sh	0.44	~1930 1922 ~1911 sh	0.41
$\nu_3 + \nu_{10}$	{ R Q P }	0.04	~1783 ~1568 sh ~1548	0.07	~1760 ~1560 sh 1542	0.04	~1784 ~1560 sh 1545	~0.05
ν_3	{ Q Q P }	14.8	1538 1533 1525	21.5	1510 1505 1495	11.5	1538 1530 1524	10.5
ν_{12}	(NO str.)	—	—	—	—	—	—	—
ν_4	{ (A'', CH_3 def.) (A', CH_3 def.) ^d }	<0.20	~1439 — 1427	—	{ ~1440 — ~1429 }	~0.21	{ 1436 — 1426 }	~0.14
			1421				1419	
			1415				~1410	

ν_5	(CH ₃ def.)	$\left\{ \begin{array}{l} R \\ Q \\ P \end{array} \right\}$	1314 1304 1295	0.85	—	1313 1303 1294	1.0	1307 1297 1290	0.91
$\nu_4; \nu_{13}$	(CD ₃ def.)	—	—	0.18	~1081 sh	—	—	—	—
ν_5	(CD ₃ def.)	—	—	0.33	~1040 1008	—	—	—	—
ν_6	(i.p. CH ₃ rock) ^e	~977 sh	<0.2	<0.15	—	~988 sh	<0.15	~981 sh	<0.15
ν_{13}	(o.p. CH ₃ rock) ^f	948 941 933 927 ~910 sh	0.33	0.33	—	947 ~936	0.33	941 934	0.22
ν_6 $2\nu_9$	(i.p. CD ₃ rock) ^e	— ~759 sh	— ~785 sh	1.2	766 750	—	—	~920 sh ~903 sh	—
ν_7	(CS str.) ^g	$\left\{ \begin{array}{l} R \\ Q \\ Q \\ P \end{array} \right\}$	~749 sh 740 731 725	0.35	741 727 ~714 sh	747 739 729 722	0.29	719 710	0.52
ν_8	(SN str.)	$\left\{ \begin{array}{l} R \\ Q \\ Q \\ P \end{array} \right\}$	654 646 635	4.3	623 615 612 ~605	642 635 632 624	4.0	~655 645 642 635	3.9
ν_9	(SNO def.)	$\left\{ \begin{array}{l} R \\ Q \\ Q \\ P \end{array} \right\}$	~383 sh 375 370 ~365 sh	4.1	~378 374 369 ~364 sh	379 373 368	4.0	383 377 371 367	5.0
ν_{10}	(CSN def.)	—	~250	~0.25	~236	~260	~0.25	~248	~0.30

^aThe abbreviation sh indicates that the band is observed as an unresolved shoulder. ^bThe relative intensities, *I*, in absorbance units have been normalized to *d* = 10 cm and *P* = 100 Torr. ^cThis overtone obscures the approximately degenerate pair of CH₃ stretches. ^dThe estimated positions of the band center for ν_4 of the normal, ¹⁵N- and ¹³C-substituted molecules are 1433, 1434, and 1429 cm⁻¹, respectively. ^ei.p. = in-plane. ^fo.p. = out-of-plane. ^g ν_7 (CS str.) and ν_{13} (o.p. CD₃ rock) are accidentally degenerate for CD₃SNO.

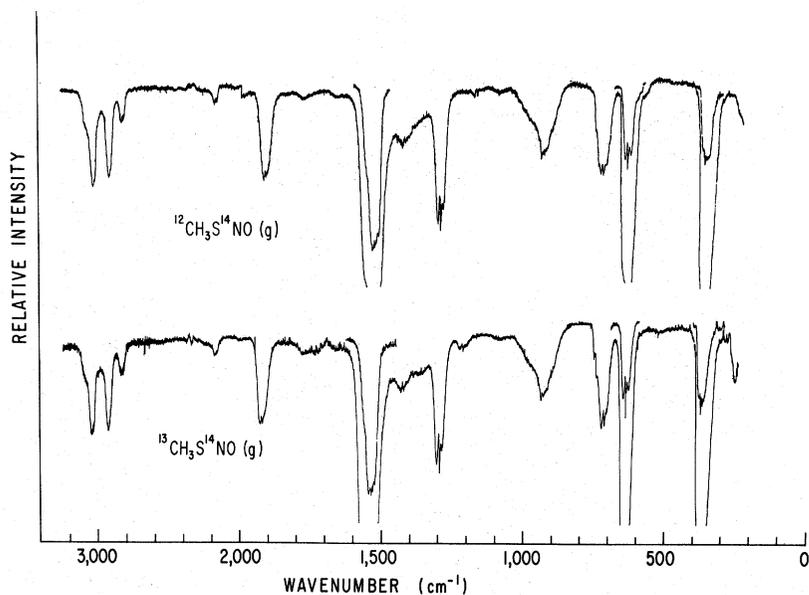


Fig. 1. Gas-phase IR spectra of $^{12}\text{CH}_3\text{S}^{14}\text{NO}$ ($P = 49.5$ and 5.2 torr) and $^{13}\text{CH}_3\text{S}^{14}\text{NO}$ ($P = 50.3$ and 6.5 torr). The very weak feature at ~ 1200 cm^{-1} apparently results from a reaction of the thionitrite with CsI window material.

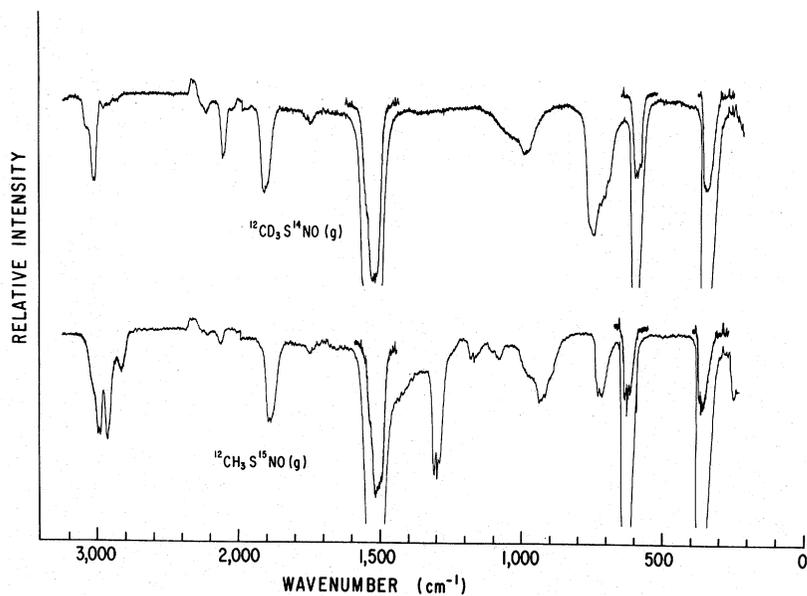


Fig. 2. Gas-phase IR spectra of $^{12}\text{CD}_3\text{S}^{14}\text{NO}$ ($P = 51.4$ and 5.9 torr) and $^{12}\text{CH}_3\text{S}^{15}\text{NO}$ ($P = 52.2$ and 5.4 torr). The two weak features at ~ 1100 and ~ 1200 cm^{-1} in the latter spectrum apparently result from a reaction of the thionitrite with the CsI window material.

lie sufficiently parallel to I_A , the smallest moment of inertia, to produce such a band shape.

Symmetry coordinates and force-field

anti-Methyl thionitrite has C_s symmetry, the four skeletal atoms and one of the hydrogens being coplanar. A seven-atom molecule of such symmetry

TABLE 2

Force constants for methyl thionitrite

Force constant	Symmetry coordinate ^a	Value ^b	Dispersion ^c
<i>A' Block</i>			
<i>Diagonal</i>			
<i>F</i> (1)	$\nu_a(\text{CH}_3)$	4.88 ^e	0.06
<i>F</i> (2)	$\nu_s(\text{CH}_3)$	4.83	0.02
<i>F</i> (3)	$\nu(\text{NO})$	10.23	0.05
<i>F</i> (4)	$\delta_a(\text{CH}_3)$	0.532 ^e	0.003
<i>F</i> (5)	$\delta_s(\text{CH}_3)$	0.559	0.014
<i>F</i> (6)	$\rho_{\parallel}(\text{CH}_3)^d$	0.632 ^e	0.005
<i>F</i> (7)	$\nu(\text{CS})$	3.24	0.04
<i>F</i> (8)	$\nu(\text{SN})$	2.9	0.4 ^g
<i>F</i> (9)	$\delta(\text{SNO})$	0.81	0.04 ^g
<i>F</i> (10)	$\delta(\text{CSN})$	1.16	0.08 ^g
<i>Interaction</i>			
<i>F</i> (16)	$\nu_s(\text{CH}_3), \delta_s(\text{CH}_3)$	-0.21	0.11
<i>F</i> (17)	$\delta_a(\text{CH}_3), \rho(\text{CH}_3)^d$	-0.014	0.009
<i>F</i> (18)	$\delta_s(\text{CH}_3), \nu(\text{CS})$	-0.37	0.04
<i>F</i> (19)	$\rho_{\parallel}(\text{CH}_3), \nu(\text{SN})$	-0.10	0.02
<i>F</i> (20)	$\nu(\text{SN}), \delta(\text{SNO})$	0.5 ^f	(0.2) ^g
<i>F</i> (21)	$\nu(\text{NO}), \delta(\text{SNO})$	0.5 ^f	(0.2) ^g
<i>A'' Block</i>			
<i>Diagonal</i>			
<i>F</i> (11)	$\nu_a(\text{CH}_3)$	4.88 ^e	0.06
<i>F</i> (12)	$\delta_a(\text{CH})$	0.532 ^e	0.003
<i>F</i> (13)	$\rho_{\perp}(\text{CH}_3)^d$	0.632 ^e	0.005
<i>F</i> (14)	$\tau(\text{CH}_3)$	—	—
<i>F</i> (15)	$\tau(\text{CS—NO})$	—	—

^a ν_a , antisym. str.; ν_s , sym. str.; δ_s , sym. bend; ρ , rock; τ , torsion. ^bUnits: stretching, mdyn \AA^{-1} ; bending and torsional, mdyn $\text{\AA} \text{rad}^{-2}$; interaction, mdyn rad^{-1} . ^cEstimated from the standard error in the frequency parameters. ^dParallel and perpendicular to the plane of symmetry. ^eThe three pairs of constants associated with the nearly degenerate modes of the methyl group were constrained so that the two constants of each pair (A' and A'') would refine to the same value. ^fInteraction constants $F(20)$ and $F(21)$ were always kept equal to one another. ^gThe estimated errors for $F(8)$, $F(9)$, $F(10)$, and $F(20) \equiv F(21)$ are from a calculation in which the two interactions were refined while fixing $F(7)$ and $F(18)$ equal to the values shown in the table.

has 15 fundamentals: $10 A' + 5 A''$. Table 2 lists the 15 primary force constants defined in terms of internal displacement coordinates: for the methyl group, symmetry coordinates identical in form to those used by Thompson and Fletcher for methyl azide [12]; for the skeletal atoms, simple stretching and deformation coordinates.

Refinement of force constants

As with most molecules, even where several isotopically substituted species are available, insufficient data preclude the calculation of an unconstrained general valence force field (GVFF). As a first approximation, just 13 diagonal constants (the two torsional constants were neglected) and one interaction constant, $F(18)$, were assigned non-zero values, and only the four primary constants associated with low-frequency ($<800 \text{ cm}^{-1}$) skeletal vibrations were refined. The initial values for the methyl group constants, and for the CS stretching coordinate were transferred from methanethiol [13]; those for the $-\text{SNO}$ moiety came from Philippe's calculation [3]; the constant for the interaction of the symmetric methyl deformation and the CS stretching coordinates was approximated by the value of the analogous interaction constant of CH_3Cl [14].

Later the remaining stretching and bending constants were included in the refinement, along with the interactions $F(19)$, $F(20)$, and $F(21)$. $F(20)$ and $F(21)$ were always held equal to one another. Unfortunately, either $F(19)$ or the pair $F(20) \equiv F(21)$ had to be kept fixed to achieve convergence. Simultaneous refinement of these three off-diagonal constants was possible only if one of the skeletal constants, such as $\nu(\text{CS})$, was made invariant. Initially, a series of numerical experiments which fixed either $F(19)$ or the pair $F(20) \equiv F(21)$ (followed by small trial-and-error changes in its value) showed that the best fit between observed and calculated frequencies and the most reasonable potential-energy distribution (PED) resulted when $F(19) = -0.10$ and $F(20) \equiv F(21) = +0.5 \text{ m dyn rad}^{-1}$. Later, these values were verified by a refinement which fixed $F(7) = 3.24 \text{ m dyn \AA}^{-1}$ and $F(14) = -0.37 \text{ m dyn rad}^{-1}$.

Fixing either interaction constant to zero, while allowing the other to refine is also unsatisfactory. In each instance, the fit between observed and calculated frequencies is much poorer and the PED for the low-frequency skeletal modes becomes unrealistically mixed or even results in an untenable transposition of vibrational assignments.

With the exception of $F(16)$ and $F(17)$, which improved the calculated methyl group frequencies, attempts to include additional interactions such as $F[\nu(\text{SN}), \nu(\text{NO})]$ proved unsuccessful. Table 2 presents the values for all the force constants calculated in the final refinement.

RESULTS AND DISCUSSION

With some exceptions, the assignments for the normal and perdeuterated molecules (Table 1) are in general accord with those in earlier publications [1–5]. The two regions where the most significant disagreement exists are the one from 3000–2800 cm^{-1} involving the CH stretching vibrations and that from 800–600 cm^{-1} containing the CS and SN stretching modes and the two CD_3 rocking vibrations.

Of the three CH stretches (ν_1 , ν_2 , and ν_{11}) only ν_2 can be assigned unequivocally in the three non-deuterated species. It occurs at 2928 cm^{-1} in the normal molecule (Fig. 1) and probably corresponds to the lone Raman band reported in this region for the neat liquid: a medium intense line at 2923 cm^{-1} [4]. The approximately degenerate pair, ν_1 and ν_{11} , is obscured by the moderately intense first overtone of the NO stretching vibration, $2\nu_3$. This overtone is observed at ~ 3039 cm^{-1} in the three ^{14}N -containing species but shifts to 2991 cm^{-1} upon ^{15}N substitution (Fig. 2). For the perdeuterated analog, the CD stretching modes absorb at 2248 cm^{-1} (ν_1 and ν_{11}) and at 2128 cm^{-1} (ν_2) (Fig. 2). The band at 2830 cm^{-1} in the normal molecule is most likely the first overtone of the nearly degenerate methyl group deformations.

More significant in terms of our future research, however, is the correct assignment of $\nu(\text{CS})$ and $\nu(\text{SN})$ (ν_7 and ν_8). Originally, Philippe tentatively proposed that these vibrations were responsible, respectively, for a weak absorption observed at 735 cm^{-1} and a moderately strong transition at 646 cm^{-1} [1]. Later, based on his calculation of a simple valence force field, he concluded that the order should be transposed [3]. Both Christensen et al. [4] and Male [5] concurred. The former provided no additional supporting data; the latter based his choice, in part, on his data for CD_3SNO . Because the lower-frequency band in the deuterated molecule shifts 33 cm^{-1} to 613 cm^{-1} , Male assumed that this feature is the one associated with $\nu(\text{CS})$. He then assigned the other skeletal stretching fundamental, by default, to a shoulder at 727 cm^{-1} on one of the two CD_3 rocking vibrations (Fig. 2). In retrospect, based on considerations other than frequency shifts alone, one concludes that Philippe's original assignment [1] is more likely the correct one.

A consideration of the expected relative intensities of $\nu(\text{CS})$ versus $\nu(\text{SN})$ offers some help. Typically, compared to CH bending modes, the CS stretch gives rise to bands of only weak to moderate intensity in other sulfur-containing organic molecules [13, 15]. By contrast, in the few IR spectra reported for compounds having a sulfur–nitrogen bond, the associated skeletal vibration generally absorbs more strongly than the CH modes do [16]. Such observations also agree with more subjective notions of the relative polarity expected for these two bond types. Because carbon and sulfur have nearly the same electronegativity, the CS bond dipole should be quite small and the associated IR band, weak. The rather large electronegativity of

nitrogen, on the other hand, would result in both a larger bond polarity for the SN bond and hence in a stronger IR absorption during the vibrational transition.

The uncertainty in assignments is ultimately resolved by the frequency shifts observed for these two modes in the ^{13}C - and ^{15}N -substituted molecules. In the former, only the weaker, higher-frequency band shifts, decreasing 16 cm^{-1} to 719 cm^{-1} . In the latter derivative, the more intense, lower-frequency absorption changes position by -13 cm^{-1} to 633 cm^{-1} . Thus, it is concluded that of these two bands the weak one at higher frequency is due to $\nu(\text{CS})$, while the strong feature at lower frequency must arise from $\nu(\text{SN})$.

The present vibrational analysis further corroborates these arguments. The calculated frequency shifts for $\nu(\text{CS})$ and $\nu(\text{SN})$ in the ^{13}C - and ^{15}N -substituted analogs agree closely with the empirical data (Table 3). The calculations also show that upon deuteration both modes decrease in frequency.

The potential-energy distribution (PED) (Table 4) provides some insight into the reasons for the marked frequency changes observed for these two vibrations upon deuterium substitution. In the case of the SN stretch, the significant coupling of this mode with the in-plane methyl rocking mode can largely account for the large deuterium isotope frequency shift. The observed decrease in frequency of $\nu(\text{CS})$ for CD_3SNO results, in part at least, from the interaction of this skeletal stretching motion and $\delta_s(\text{CH}_3)$.

Two other interactions involving skeletal vibrations appear to be of special significance. One is that between $\delta(\text{SNO})$ and $\nu(\text{SN})$ [and also $\nu(\text{NO})$]; the

TABLE 3

Observed and calculated frequencies for four isotopomers of methyl thionitrite (cm^{-1})

Assignment	CH_3SNO		CD_3SNO		$\text{CH}_3^{15}\text{NO}$		$^{13}\text{CH}_3\text{SNO}$	
	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.	Obsd.	Calc.
A_1 ν_1 [$\nu_a(\text{CH}_3)$]	— ^a	3013	2246	2247	— ^a	3013	— ^a	3001
ν_2 [$\nu_s(\text{CH}_3)$]	2928	2930	2128	2120	2926	2930	2926	2925
ν_3 [$\nu(\text{NO})$]	1535	1534	1533	1534	1507	1506	1533	1534
ν_4 [$\delta_a(\text{CH}_3)$]	1433	1433	1040	1034	1434	1433	1429	1431
ν_5 [$\delta_s(\text{CH}_3)$]	1304	1307	1008	992	1303	1307	1297	1301
ν_6 [$\rho_{\parallel}(\text{CH}_3)$]	977	973	766	769	(981) ^b	972	(980) ^b	967
ν_7 [$\nu(\text{CS})$]	735	742	727	702	734	742	719	726
ν_8 [$\nu(\text{SN})$]	646	645	613	615	633	631	643	644
ν_9 [$\delta(\text{SNO})$]	373	375	372	370	371	372	374	373
ν_{10} [$\delta(\text{CSN})$]	250	254	236	237	260	253	248	251
A_2 ν_{11} [$\nu_a(\text{CH}_3)$]	— ^a	3012	2246	2245	— ^a	3013	— ^a	3000
ν_{12} [$\delta_a(\text{CH}_3)$]	1439	1441	1040	1037	1440	1441	1436	1439
ν_{13} [$\rho_{\perp}(\text{CH}_3)$]	948	950	727	717	947	950	941	945

^a ν_1 [$\nu_a(\text{CH}_3)$] is obscured by $2\nu_3$ in the protonated species. ^bThis frequency was not included in the final refinement because of the large uncertainty in its value.

TABLE 4

Potential-energy distribution (PED)^a

Band	CH ₃ SNO ^{b,c}	CD ₃ SNO ^c
A'	ν_1 1(100)	1(98)
	ν_2 2(98)	2(95), 16(3)
	ν_3 3(98)	3(98)
	ν_4 4(95), 6(6)	4(97), 6(3)
	ν_5 5(108), 2(4), 7(3), 18(-10), 16(-5)	5(107), 2(6), 7(16), 18(-22), 16(-7)
	ν_6 6(88), 4(4), 8(3)	6(65), 8(24), 10(5), 9(3), 19(6), 20(-6)
	ν_7 7(100), 18(-6)	7(85), 18(6)
	ν_8 8(101), 9(17), 6(6), 10(4), 20(-30), 19(-4)	8(80), 6(30), 9(16), 20(-25), 19(-7)
	ν_9 9(74), 10(13), 7(4), 20(7)	9(77), 10(10), 7(4), 20(7)
	ν_{10} 10(78), 9(23), 20(-8)	10(88), 9(19), 20(-7)
A''	ν_{11} 11(100)	11(99)
	ν_{12} 12(93), 13(7)	12(96), 13(4)
	ν_{13} 13(93), 12(7)	13(96), 12(3)

^aContributions of less than 3% have been omitted. ^bThe PED for CH₃SNO, CH₃S¹⁵NO, and ¹³CH₃SNO are virtually identical. ^cThe first number designates the force constant; the second (in parentheses), its % PED.

other is the mixing of δ (SNO) and δ (CSN). In the first instance, inclusion of the appropriate interaction constants, $F(20) = F(21)$, is required to obtain a satisfactory set of calculated frequencies and a reasonable PED. For the latter case, attempts to refine the interaction constant involving these two skeletal deformations proved impossible. The data set is simply insufficient, as there are no data for molecules with isotopic substitution at the sulfur and oxygen atoms.

Despite these conspicuous limitations, the force field presented here offers a means of comparing the spectroscopic properties of this molecule with other similar compounds. Table 5 gives the observed frequencies for the skeletal vibrations of CH₃SNO and two related species, CF₃SNO [17] and *anti*-CH₃ONO [18, 19]. It is interesting to note the dramatic frequency changes observed for ν (NO) for these molecules. Apparently, this is not simply a function of the mass difference between sulfur and oxygen, for ν (NO) has almost as high a value in CF₃SNO [17] as in CH₃ONO [18, 19]; nor is it correlated with stability: both thionitrites are less stable than the corresponding nitrite.

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TABLE 5

Comparisons between the observed gas-phase frequencies (cm^{-1}) of the skeletal modes for two thionitrites and a nitrite

Coordinate ^a	CH ₃ SNO	CF ₃ SNO ^b	<i>anti</i> -CH ₃ ONO ^c
$\nu(\text{NO})$	1535 vs	1660 vs	1677 vs
$\nu(\text{CY})$	735 w	753 ms	1046 m
$\nu(\text{YN})$	646 s	629 vs	812 vs
$\delta(\text{YNO})$	375 s	430 s	565 s
$\delta(\text{CYN})$	~250 m	[236] ^d	~365 w

^aFor the thionitrite species, Y = S; for CH₃ONO, Y = O. ^bObserved frequencies from ref. 17. New, tentative assignments based on the present study. ^cThe assignments and observed frequencies given here are stated in ref. 18 to be for the *syn*-conformation. Ref. 19 reports that these are actually due to *anti*-CH₃ONO. ^dPosition estimated from overtone and combination bands (ref. 17).

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