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early part of this work is in W. H. Miller, Accts. Chem. Res. **4**, 161 (1971).

[2] Also see the related work by (a) R. A. Marcus. Chem. Phys. Letters **7**, 525 (1970); (b) R. A. Marcus, J. Chem. Phys. **54**, 3965 (1971); (c) J. N. L. Connor and R. A. Marcus, *ibid.* **55**, 5636 (1971); (d) W. H. Wong and R. A. Marcus, *ibid.* **55**, 5663 (1971); (e) R. A. Marcus, *ibid.* **56**, 311 (1972); (f) **56**, 3548 (1972).

[3] Some other recent work also dealing with the use of classical mechanical methods in collision theory is (a) P. Pechukas, Phys. Rev. **181**, 166, 174 (1969); (b) J. C. Y. Chen and K. M. Watson, *ibid.* **188**, 236 (1969); (c) R. E. Olson and F. T. Smith, Phys. Rev. A **3**, 1607 (1971); (d) R. J. Cross, Jr., J. Chem. Phys. **52**, 5703 (1970); (e) B. C. Eu, *ibid.* **52**, 3903 (1970); (f) M. D. Pattengill, C. F. Curtiss, and R. B. Bernstein, *ibid.* **54**, 2197 (1971); (g) R. D. Levine and B. R. Johnson, Chem. Phys. Letters **7**, 404 (1970); (h) I. C. Percival and D. Richards, J. Phys. B **3**, 315, 1035 (1970); (i) I. L. Beigman, L. A. Vainshtein, and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **57**, 1703 (1969) [Sov. Phys. JETP **30**, 920 (1970)].

[4] See, for example, E. A. Mason and L. Monchick, Advan. Chem. Phys. **12**, 351 (1967).

[5] M. G. Gutzwiller, J. Math. Phys. **12**, 343 (1971).

[6] W. H. Miller, J. Chem. Phys. **56**, 38 (1972).

[7] J. B. Keller, Ann. Phys. (N.Y.) **9**, 24 (1960).

[8] P. Pechukas, J. Chem. Phys. **54**, 3864 (1971); P. Pechukas (unpublished).

[9] See, for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1958), p. 158ff.

[10] See, for example, A. Messiah, *Quantum Mechanics* (Wiley, New York, 1962), pp. 712–720.

[11] E. P. Wigner, Phys. Rev. **40**, 479 (1932).

[12] Y. Hahn and K. M. Watson, Phys. Rev. A **6**, 548 (1972).

[13] I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic, New York, 1965).

[14] Ref. 13, p. 940.

[15] M. Born, *The Mechanics of The Atom* (Ungar, New York, 1960), pp. 286–292.

[16] See, for example, E. A. Hylleraas, Advan. Quantum Chem. **1**, 1–33 (1964).

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Vibrational Spectrum of Methanetellurol*

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The infrared and Raman spectra of methanetellurol have been investigated with the aid of the isotopic species CH_3TeD, CD_3TeH, CD_3TeD. Spectra of vapor, liquid, and matrix isolated samples are presented. The spectra of the molecule are consistent with the expected C_s symmetry and resemble those of a near symmetric top molecule. Normal coordinate calculations were conducted and results are reported and compared with similar molecules. Unfortunately, repeated attempts to observe the torsional motion in both solid matrix and vapor were unsuccessful.

INTRODUCTION

The origin of nonbonded interactions has captured the interest of chemists for many years and the magnitude of the barrier hindering internal rotation is a measure of these interactions. In the series of molecules CH_3MH_2 or CH_3MH where M is a group V or VI atom, it has been concluded[1] that the barriers in the CH_3MH_2 molecules are simply the sums of the individual M–H barriers (the barriers in the corresponding CH_3MH molecules) and that the nonbonded electrons contribute little to the overall observed barrier. This study extends from the first pair in the series (CH_3NH_2, CH_3OH) to the pair CH_3AsH_2, CH_3SeH. The impetus for a study of the vibrational spectrum of CH_3TeH was to see if the previous effects of nonbonded interactions exist for very large M atoms where *d*- and *f*-electron participation may play an important role in the bonding. Unfortunately, as will be shown later, the torsional vibration in CH_3TeH could not be found. Hence, we report here only a vibrational analysis of the molecule and a normal coordinate calculation which excludes the torsional vibration.

The only reference to methanetellurol in the literature is a method of synthesis reported by Baroni.[2] This report also details a few important properties of methanetellurol and other organotellurium hydrides. Since there are no structural data available for methanetellurol, the geometry has been assumed to be similar to the related CH_3SH,[3] CH_3SeH,[4] and H_2Te[5] molecules. On assumption of the geometry having C_s symmetry (Fig. 1), it is found (see Table I) that the axis of least inertia lies very near to the carbon–tellurium bond and approximates the symmetry axis of a prolate symmetric top. The axis of intermediate inertia lies in the plane of the molecule and approximately perpendicular to the carbon–tellurium bond, while the axis of greatest inertia lies perpendicular to the plane of symmetry. Therefore, the vibrations of CH_3TeH will be either symmetric (A') or antisymmetric (A'') with respect to the plane of symmetry. The A'' vibrations will be similar to perpendicular bands in the symmetric top approximation; type *C* in the asymmetric-top case. The A' vibrations will be either parallel (Type *A*) or perpendicular (Type *B*), depending on the direction of the changing dipole. Type *A* occurs if the dipole change lies nearly parallel to the carbon tellurium bond axis and Type *B* if the dipole change lies along the *B* axis. Since the tellurium atom is so large, the overall methyl group spectrum is expected to be analogous to that of the CH_3I molecule. On the other hand, the lower symmetry of the CH_3TeH molecule gives rise to considerable mixing of the vibrational modes and therefore a simple description of these modes is not always possible. This is especially evident in the methyl wagging (or rocking) mode, since considerable mixing of the A' wag with the C–Te–H bending motion is expected.[6]

EXPERIMENTAL

A preparation of methanetellurol has been reported[2] but for convenience we chose to synthesize the material by a method similar to CH_3SeH.[4] In this method, dimethyl ditelluride[7] is dissolved in liquid ammonia and is reduced with sodium metal. The ammonia is evaporated and the container is evacuated to insure the complete removal of the ammonia. The remaining solid is cooled in a dry ice bath and is then treated with 10% phosphoric acid (sulfuric acid was found to oxidize the hydride). The vessel is pumped continuously and allowed to warm slowly to allow melting of the aqueous acid. Upon melting, the acid reacts with the residue (CH_3TeNa) to give methanetellurol, which is collected in a trap cooled by liquid N_2. It should be noted that even with weak oxidizing acids there is always some decomposition to elemental tellurium and reconversion to dimethyl ditelluride. Since this amount of decomposition is unpredictable, the yields vary greatly from experiment to experiment. The product was dried over P_2O_5 and purified by bulb-to-bulb distillation. No impurities could be detected in the infrared spectrum but the Raman spectrum always showed evidence of $(CH_3Te)_2$ by the presence of a weak line near 190 cm^{-1} which is due to the stretching of the Te–Te bond.[8] Since the tellurol readily decomposes to the ditelluride on standing at room temperature, it was impossible to remove the last traces of this impurity. Moreover, it was imperative that all samples be stored at liquid nitrogen temperature in the absence of air.

The corresponding CD_3TeH sample was prepared in a similar manner using $(CD_3Te)_2$ for starting material. Compounds with deuterium on the tellurium atom (CH_3TeD and CD_3TeD) were prepared from the corresponding CH_3TeH and CD_3TeH samples by exchanging at least twice with D_2O and subsequent distillation. Because of the small size of the samples and the apparent ease with which it exchanges, it was never possible to obtain complete deuteration of the Te atom. However, sufficient exchange could be obtained to observe the spectra. Bands arising from the unexchanged products could easily be identified from the spectra of these pure compounds. No difficulty was encountered in identifying the spectral bands arising from the CH_3TeD and CD_3TeD species.

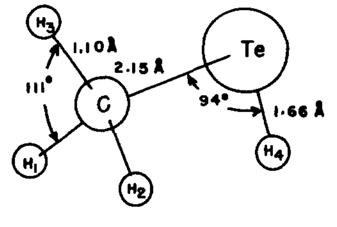

FIG. 1. Assumed structure of CH_3TeH.

TABLE I. Principal moments of inertia of methanetellurol.[a]

	I_A	I_B	I_C
CH_3TeH	68.29	5.99	71.03
CH_3TeD	68.43	8.68	73.86
CD_3TeH	85.08	9.24	87.82
CD_3TeD	85.26	11.93	90.68

[a] Units in amu·Å^2 calculated from assumed structure (see Fig. 1). The values represent a sum of isotopic (tellurium) moments weighted by the natural abundance of each.

The methanetellurol obtained was always a pale yellow volatile liquid. This color is likely caused by small impurities of the deep red-colored dimethylditelluride.[8] Similar to the analogous S [3] and Se [4] compounds, CH_3TeH has a very obnoxious and persistent odor. However, it seems to be considerably more unstable and readily decomposes at room temperature. This decomposition is readily catalyzed by stopcock grease and therefore all valves should be of a greaseless type. It reacts immediately with oxygen.

The Raman spectra (see Figs. 2 and 3) were obtained on a conventional Cary 81 spectrophotometer equipped with a He–Ne laser excitation source. Despite the long wavelength (632.8 nm), irradiation of the room temperature samples contained in Pyrex capillaries accelerated the rate of decomposition and rapidly formed troublesome bubbles which at times caused sufficient increase in pressure to break the capillary tube. Decomposition could be reduced by cooling the liquid samples to approximately −40°C to −50°C with a stream of N_2 gas which had been precooled by passing it through liquid nitrogen. The decomposition seemed to follow two paths: one in which $(CH_3Te)_2$ and H_2 are formed, and the other which occurs mainly in the gas phase where CH_4, higher organics, H_2, and a Te mirror are produced.

The mid-infrared spectrum (see Fig. 4) of CH_3TeH vapor at 100 torr was observed with the aid of a Beckman IR-12 infrared spectrophotometer. The use of conventional gas cells had to be discarded because of serious decomposition on the usual sealants. Thus, a small, inert, easily demountable gas cell was developed.[9] This cell has all Viton O-ring seals and is Teflon coated to increase its inertness. The infrared spectra of the vapors of the deuterated samples were not attempted since only small quantities were available and exchange with the cell makes it difficult to maintain complete deuteration at the Te atom.

The mid-infrared spectra of the matrix isolated samples were also obtained. The temperature of liquid hydrogen was maintained with an Air Products Cryotip operated from gaseous H_2 and N_2. The samples were diluted with high-purity Ar in the ratio of 100–1000:1,

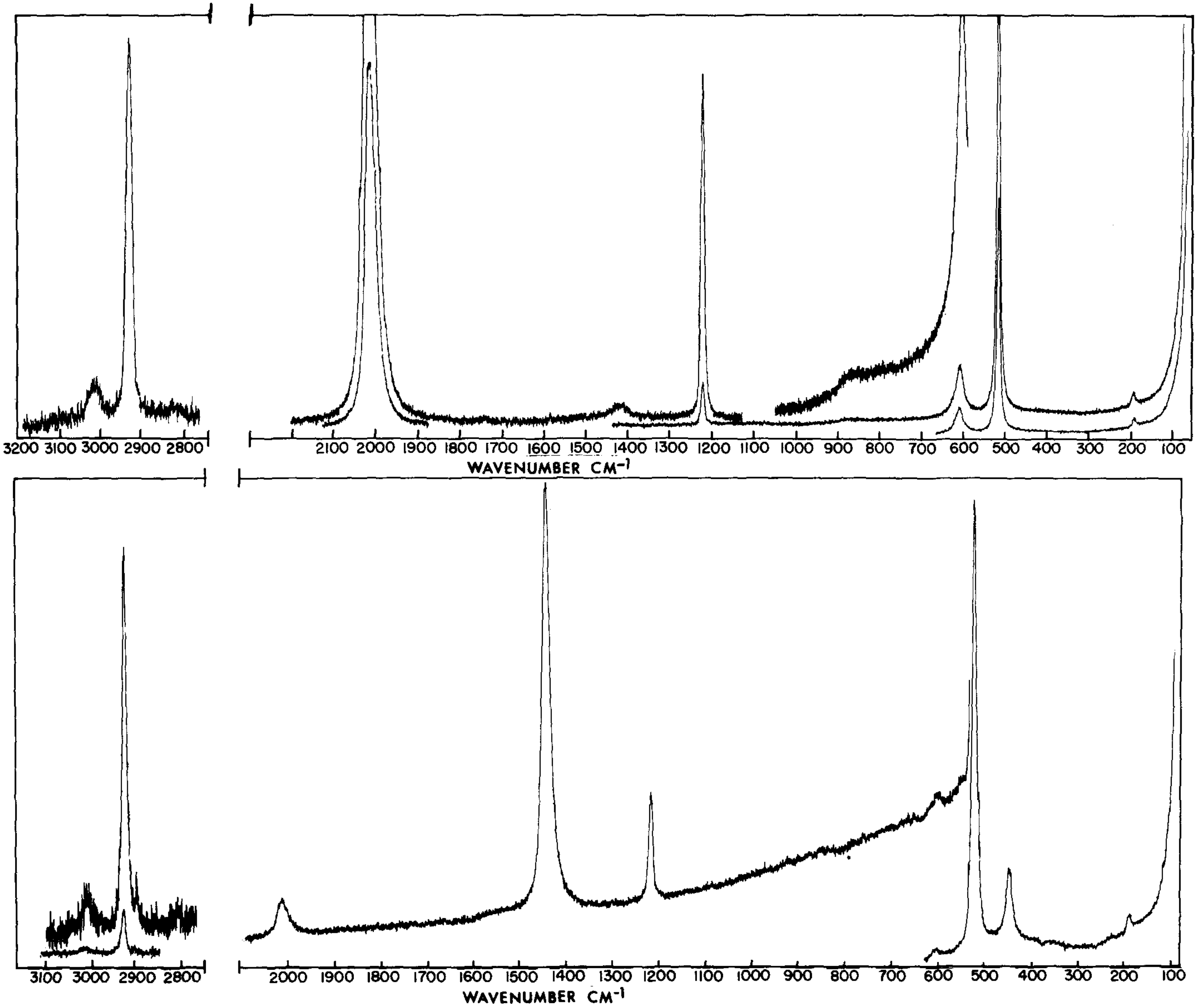

FIG. 2. Raman spectra of liquid CH_3TeH (upper trace) and liquid CH_3TeD (lower trace).

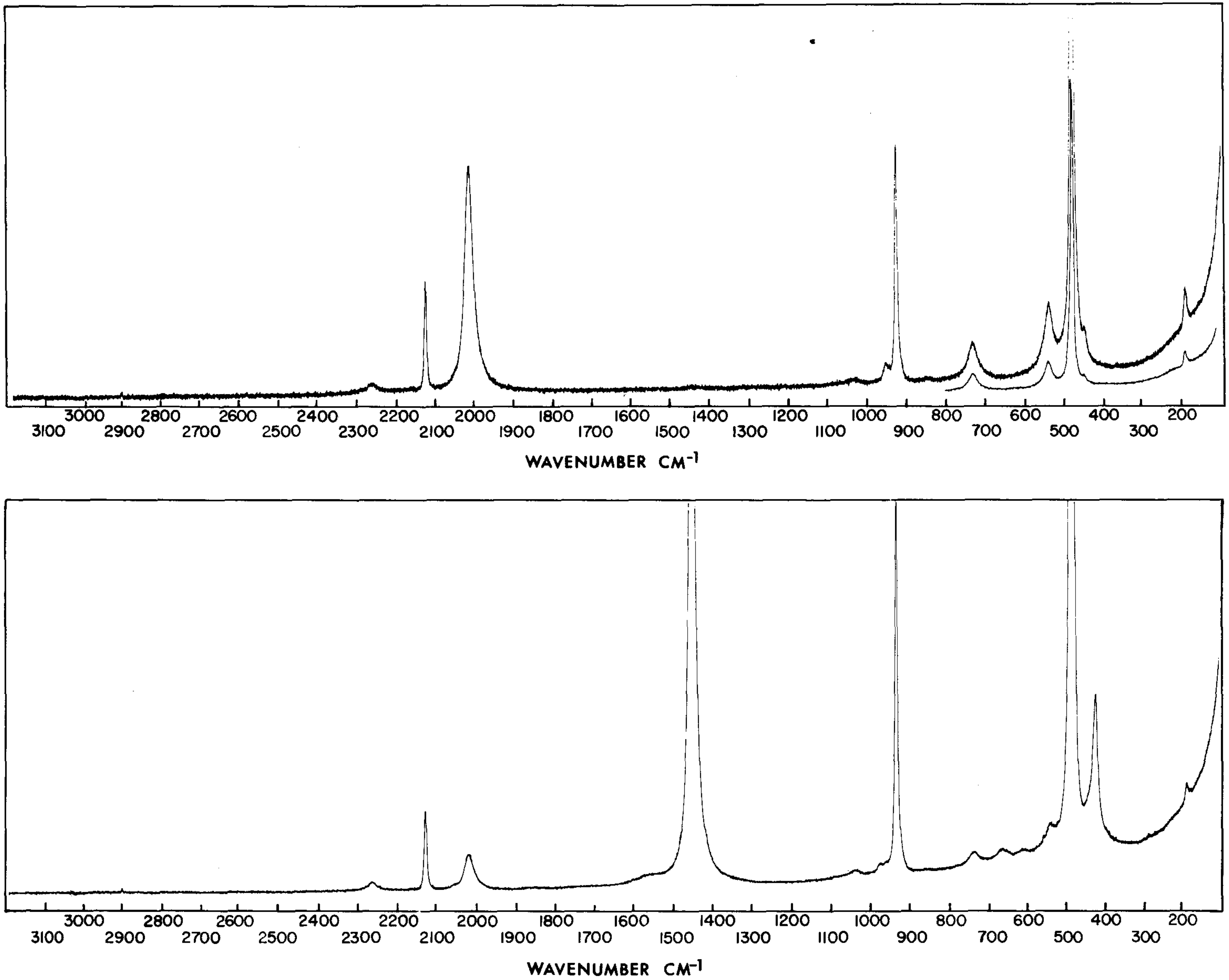

FIG. 3. Raman spectra of liquid CD_3TeH (upper trace) and liquid CD_3TeD (lower trace).

argon:sample. Dilutions of at least 500 to 1 were required to obtain true matrix isolated samples. Because of the long deposition times required, some sample decomposition occurred and was evident due to the Te metal deposited on associated glassware. This decomposition made it impossible to maintain constant dilutions but concentrations were in the ranges given above. It should be noted that because of the lability of the hydrogen bonded to tellurium, it was not possible to observe the spectrum of CH_3TeD or CD_3TeD in the absence of CH_3TeH and CD_3TeH, respectively. However, the spectra of the matrix isolated molecules are so linelike that the spectrum of CH_3TeH or CD_3TeH could be accounted for readily in the spectrum of the corresponding tellurium-deuterated samples and the new lines are attributed to the latter molecules. Many of the fundamentals are accidentally degenerate and show no splitting in the combined spectrum. However, the fundamentals that involve motion of the hydrogen bonded to the tellurium show some shift on isotopic substitution and can easily be identified in the combined spectrum. This technique also allowed the separation of nearly degenerate bands and greatly facilitated the vibrational assignments.

Numerous attempts were made to observe a torsional fundamental for CH_3TeH but all were without success. These included sampling in the gas, solid and matrix isolated states and with dispersive and nondispersive instrumentation, but no indication of a torsional fundamental was ever observed.

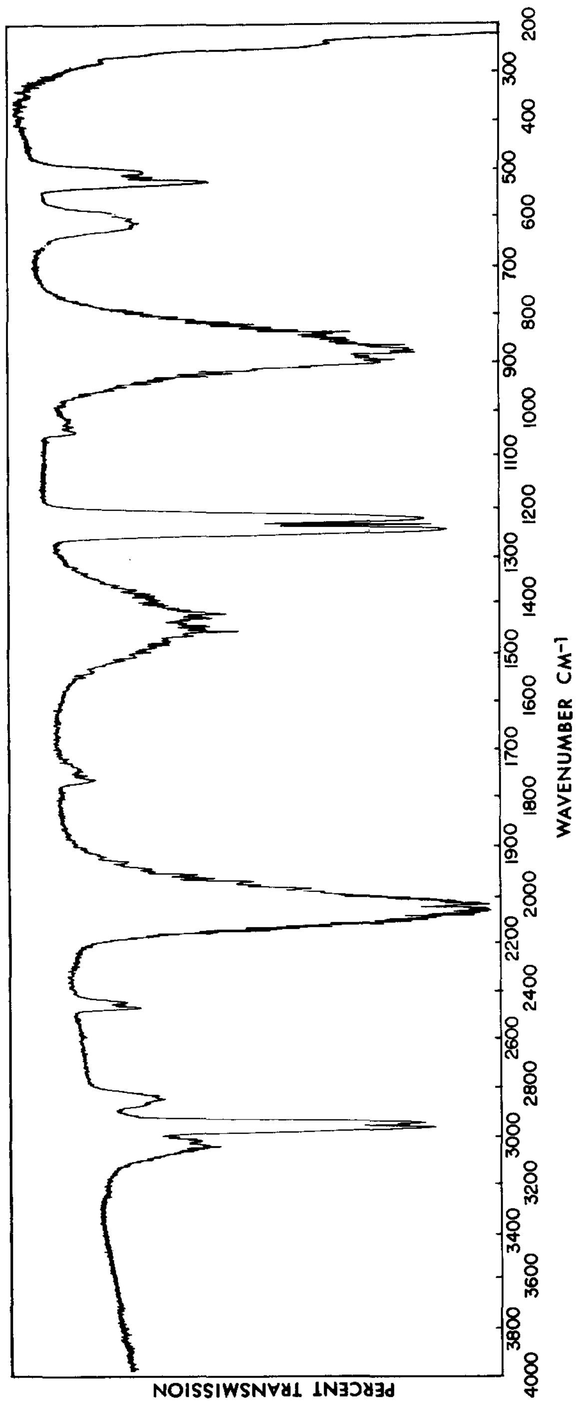

FIG. 4. Infrared spectrum of CH_3TeH vapor.

ASSIGNMENTS OF FUNDAMENTALS

Methanetullurol is expected to have C_s symmetry like the corresponding Se[4] and S[3] molecules. Therefore, the spectrum of CH_3TeH and each of its deuterated analogues should have close similarities with the spectra of these molecules, particularly methaneselenol. In a molecule with such low symmetry all vibrations are both infrared and Raman allowed. For CH_3TeH the twelve fundamental modes are divided as follows: eight A' modes which can give rise to polarized Raman lines and four A'' modes which should be Raman depolarized. Because of the limited amounts of the deuterated samples available and the relatively large amounts of sample needed for gas phase work, infrared spectra for the vapor are illustrated in Fig. 4 for CH_3TeH only. There is a very close resemblance of this spectrum to that of CH_3SeH[4] in the gas phase, with one striking exception: the C–Se stretching fundamental was not observed directly for CH_3SeH but, in contrast, the C–Te stretching mode gives rise to a fairly intense band (A type) centered near 520 cm^{-1}. Due to the close resemblance of the Raman spectra of the Se and Te compounds, assignments of the fundamental vibrational frequencies can easily be made with great certainty by simple comparison. Thus, a detailed discussion of all the assignments is not necessary and they will be discussed only briefly. In subsequent discussion,

TABLE II. Symmetry coordinates for methanetellurol.

	A' Species
CH_3 antisym st	$S_1 = 6^{-1/2}(\Delta r_1 + \Delta r_2 - 2\Delta r_3)$
CH_3 sym st	$S_2 = 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3)$
TeH st	$S_3 = \Delta R$
CH_3 antisym def	$S_4 = 6^{-1/2}(\Delta\alpha_1 + \Delta\alpha_2 - 2\Delta\alpha_3)$
CH_3 sym def[a]	$S_5 = N^{-1/2}[A(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - B(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$
CH_3 rock	$S_6 = 6^{-1/2}(\Delta\beta_1 + \Delta\beta_2 - 2\Delta\beta_3)$
C–Te–H bend	$S_7 = \Delta\theta$
C–Te st	$S_8 = \Delta D$
Redundancy[a]	$S_9 = N^{-1/2}[B(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) + A(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$
	A'' Species
CH_3 antisym st	$S_{10} = 2^{-1/2}(\Delta r_1 - \Delta r_2)$
CH_3 antisym def	$S_{11} = 2^{-1/2}(\Delta\alpha_1 - \Delta\alpha_2)$
CH_3 rock	$S_{12} = 2^{-1/2}(\Delta\beta_1 - \Delta\beta_2)$

[a] $A = \sqrt{3}\cos\beta = 0.5472$; $B = \cos\alpha/2 = 0.5699$; $N = (3A^2 + 3B^2)$.

frequencies are those observed in the Raman spectra unless otherwise stated.

Methyl Fundamentals

Because of the low symmetry of the CH_3TeH molecule, it is possible that three lines might be observed in each spectrum corresponding to the three possible CH_3 stretching vibrations. Two would be A' and one A''. However, due to the large mass of the tellurium atom, the molecule is expected to behave like a symmetric top molecule which would give rise to two methyl stretching fundamentals, one of which is doubly degenerate. In each case only two Raman lines were observed in the expected region. For CH_3TeH and CH_3TeD, respectively, these were observed at 2931 cm^{-1} and 2929 cm^{-1} for the polarized lines (A') and at 3019 cm^{-1} and 3012 cm^{-1} for the depolarized lines (A''). The corresponding lines of CD_3TeH and CD_3TeD were at 2126 cm^{-1} and 2127 cm^{-1} and at 2263 cm^{-1} and 2262 cm^{-1}.

The next vibrational frequencies associated with the fundamentals of the methyl group are the deformation vibrations. As before under the low-molecular symmetry, it is possible to have three fundamental frequencies. However, as in the case of the CH_3 stretching modes, only two lines are observed in the expected region. The polarized lines (A') at 1220 cm^{-1}, 1219 cm^{-1}, 928 cm^{-1}, and 930 cm^{-1} are assigned to the CH_3 symmetric deformations of CH_3TeH, CH_3TeD, CD_3TeH, and CD_3TeD, respectively. Depolarized lines are found at 1417 cm^{-1} for CH_3TeH and at 1034 and 1032 cm^{-1} for CD_3TeH and CD_3TeD, respectively. The methyl deformation of CH_3TeD was not observed due to the overlapping of the strong line at 1449 cm^{-1} arising from the TeD stretching fundamental. For the calculations this fundamental is estimated to be at 1415 cm^{-1}.

Methyl Rocking and Te–H Bending Fundamentals

These fundamentals are strongly mixed and any discussion must include both types of vibrations. Under C_s symmetry these three fundamentals can be classified according to the following species: CH_3 in-plane rock and C–Te–H bending are in class A', and the CH_3 out-of-plane rock in class A''. As in CH_3SeH,[4] the in-plane methyl rock can couple with the C–Te–H bending, causing considerable separation of the two rocking modes. Thus, the in-plane methyl rocking fundamental is expected to be found at higher wavenumber than the out-of-plane methyl rock and the C–Te–H bend is expected to be somewhat lower frequency. This repulsion of the TeH bend and the A' methyl rock should be especially pronounced in the CD_3TeH molecule because the two fundamentals are expected to be in the same spectral region in the absence of strong interaction. This is demonstrated in the spectra of the matrix isolated samples where the splittings are observed to be 20 cm^{-1} ($A' = 868$ cm^{-1}, $A'' = 848$ cm^{-1}); 8 cm^{-1} ($A' = 856$ cm^{-1}, $A'' = 848$ cm^{-1}); 110 cm^{-1} ($A' = 736$ cm^{-1}, $A'' = 626$ cm^{-1}), and 39 cm^{-1} ($A' = 665$ cm^{-1} and $A'' = 626$ cm^{-1}) for CH_3TeH, CH_3TeD, CD_3TeH, and CD_3TeD, respectively. The C–Te–H bending is also affected upon deuteration of the methyl group. It is lowered to 541 cm^{-1} in CD_3TeH from 608 cm^{-1} in CH_3TeH and in the corresponding TeD molecules the shift is from 447 cm^{-1} to 425 cm^{-1} in going from CD_3TeH to CD_3TeD. Again, the most pronounced interaction is in the CD_3TeH molecule.

C–Te Stretching Fundamental

The C–Te stretching vibration and the C–Te–H bending mode are expected in the same spectral region. Since these fundamentals are both of A' species there should be some mixing of the vibrations. Thus, there should be a marked effect on the C–Te stretch upon deuteration. In CH_3TeH the C–Te–H bending falls at higher wavenumber than the C–Te stretch, and any interaction would be expected to push the C–Te stretch to lower wavenumber. For CH_3TeD the opposite is expected to occur since the C–Te–D bend is of lower frequency than the C–Te stretch for this molecule and any interaction is expected to move the bending down and the C–Te stretching up. Hence, the C–Te stretch is observed as polarized lines at 516 cm^{-1} and 525 cm^{-1} for the CH_3TeH and CH_3TeD pair, respectively. For the deuteromethyl molecules the coupling with the methyl deformations moves both C–Te stretching fundamentals to lower wavenumbers but the reversal is again present in this pair. The C–Te stretches are assigned to the polarized lines at 479 cm^{-1} for CD_3TeH and at 487 cm^{-1} for CD_3TeD. These values are in agreement with those observed for the C–Te stretching fundamentals of $CD_3TeTeCD_3$ and $CH_3TeTeCH_3$, which were observed at 475 cm^{-1} and 509 cm^{-1}, respectively,[8] and at 528 cm^{-1} in CH_3TeCH_3.[10]

TABLE III. Observed and calculated fundamental frequencies (cm^{-1}) for methanetellurol.

Vib. No.	Approximate description	Observed infrared vapor	Observed Raman liquid	Calculated Raman liquid	Observed infrared matrix	Calculated infrared matrix
			A′ Species			
ν_1	CH_3 antisym st	3025	3019[a]	3021	3017	3021
			3012	3021	3017[b]	3021
			2263	2252	2260	2252
			2262	2251	2260[b]	2252
ν_2	CH_3 sym st	2956	2931	2937	2928	2935
			2929	2937	2928[b]	2935
			2126	2107	2124	2104
			2127	2107	2124[b]	2104
ν_3	Te–H st	2053	2016	2021	1990	1994
			1449	1435	1430	1422
			2107	2021	1990	1994
			1449	1435	1430	1416
ν_4	CH_3 antisym def	1437	1417	1419	1422	1422
			(1415)[c]	1419	1422[b]	1415
			1034	1025	1036	1028
			1032	1025	1036[b]	1028
ν_5	CH_3 sym def	1237	1220	1218	1215	1214
			1219	1218	1215[b]	1214
			928	932	928[b]	931
			930	932	928[b]	931
ν_6	CH_3 rock	892	870	885	868	878
			(858)	867	856	861
			733	720	736	729
			663	663	665	658
ν_7	C–Te–H bend	614	608	608	637	638
			447	447	466	469
			541	552	563	567
			425	430	444	450
ν_8	C–Te st	520	516	522	518	521
			525	524	518	529
			479	481	484	480
			487	483	487	483
			A″ Species			
ν_9	CH_3 antisym st	3025	3019	3020	3017	3020
			3012	3020	3017[b]	3020
			2263	2250	2260	2250
			2262	2250	2260[b]	2250
ν_{10}	CH_3 antisym def	1437	1417	1420	1414	1423
			1415	1420	1414[b]	1423
			1034	1025	1031	1028
			1032	1025	1031[b]	1028
ν_{11}	CH_3 rock	848	(850)	850	848	843
			(850)	850	848[b]	843
			(610)	630	626	625
			610	630	626[b]	625
ν_{12}	Torsion	···	···	···	···	···

[a] Frequencies listed in order CH_3TeH, CH_3TeD, CD_3TeH, and CD_3TeD, respectively.

[b] Denotes frequencies not directly observed and assumed to be the same as the corresponding TeH molecules since no splitting was observed in the spectra of the matrix isolated mixtures.

[c] ( ) denotes estimated frequencies.

TABLE IV. Potential-energy distribution.

Vib. No.[a]	K_{11}[b]	K_{22}	K_{33}	K_{44}	K_{55}	K_{66}	K_{77}	K_{88}	K_{58}	K_{67}
ν_1	100[c]									
	100									
	99			1						
	99			1						
ν_2		100								
		100								
		99								
		99								
ν_3			100							
			100							
			100							
			100							
ν_4				96		4				
				96		4				
				97		2				
				97		2				
ν_5					106			3	−9	
					106			3	−9	
					105			11	−17	
					105			11	−17	
ν_6				3		79	8		9	
				4		89	2		5	
						38	46		15	
						79	9		10	
ν_7						20	94	1		−15
						10	100	1		−10
						63	56			−21
						21	91	3		−15
ν_8							1	102	−4	
							1	102	−4	
							1	94	5	
						1	3	91	4	1
ν_9	100									
	100									
	99			1						
	99			1						
ν_{10}				96		4				
				96		4				
				97		2				
				97		2				
ν_{11}				4		96				
				4		96				
				2		98				
				2		98				

[a] See Table III.

[b] See Table V.

[c] Listed in order CH_3TeH, CH_3TeD, CD_3TeH, and CD_3TeD; units in percent.

TABLE V. Force constants for methanetellurol and methaneselenol.

Vibration	Constant No.[a]	CH_3SeH	CH_3TeH
(1) CH_3 antisym stretching	K_{11}	4.89	4.85
(2) CH_3 sym stretching	K_{22}	4.86	4.97
(3) M–H stretching	K_{33}	3.20	2.41
(4) CH_3 antisym deformation	K_{44}	0.53	0.51
(5) CH_3 sym deformation	K_{55}	0.61	0.48
(6) CH_3 rock	K_{66}	0.58	0.51
(7) C–M–H bending	K_{77}	0.77	0.64
(8) C–M stretching	K_{88}	2.62	2.18
(9) Interaction (6–7)	K_{67}	−0.14	0.101
(10) Interaction (5–8)	K_{58}	−0.26	−0.246

[a] Stretching force constants are given in millidynes/angstrom, bending constants in millidyne·angstrom.

TeH Stretching Mode

The tellurium hydrogen stretching fundamental is easily identified with the strong polarized Raman line at 2016 cm^{-1} in the spectrum of CH_3TeH and is observed at 2017 cm^{-1} for CD_3TeH. This indicates, as expected, that this fundamental does not couple with other fundamentals of A' species because the large Te atom isolates this motion and coupling with the methyl fundamentals does not occur. This is especially evident in the CH_3TeD molecule where the TeD stretch and the CH_3 symmetric deformation are in the same spectral region, and yet no coupling is apparent since the TeD stretching fundamental occurs at 1449 cm^{-1} for both the CH_3TeD and CD_3TeD molecules.

NORMAL COORDINATE CALCULATIONS

To compare the soundness of our assignments with those reported earlier for the sulfur[3] and selenium[4] analogues, a force field calculation was carried out. The assumed geometry is similar to the CH_3Te moiety in $CH_3TeTeCH_3$. The C–Te–H angle is assumed to be 94°. The actual values for the assumed bond angles and bond lengths are given in Fig. 1. The calculations were performed on a CDC-3800 computer with programs written by Snyder and Schachtschneider.[11,12] The method employs the Wilson FG matrix method[13] and the symmetry coordinates used are listed in Table II. Good agreement between observed and calculated spectra was obtained for the frequencies observed for both the Raman spectra of the liquid samples and the infrared spectra of the matrix isolated samples. Table III lists the observed and calculated frequencies for the four isotopic species, including both infrared and Raman data. The potential energy distribution is listed in Table IV and the MVFF force constants are listed in Table V, which compares these force constants to those of the corresponding selenium compound.

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[1] A. B. Harvey, J. Phys. Chem. **70,** 3370 (1966).

[2] A. Baroni, Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. Nat. **27,** 238 (1938).

[3] T. Kojima, J. Phys. Soc. Japan **15,** 1284 (1960). T. Pederson, P. Seibt, and C. R. Wade, "Microwave Rotational Spectrum and Internal Rotation in Methyl Mercaptan," Twenty-fifth Symposium on Molecular Structure and Spectroscopy, Ohio State Univ., 8 Sept. 1970, Paper C6.

[4] A. B. Harvey and M. K. Wilson, J. Chem. Phys. **45,** 678 (1966). Synthesis of CH_3SeH: G. E. Coates, J. Chem. Soc. **1953,** 2839.

[5] T. H. Edwards, "Analysis of Infrared Absorption Spectra of Asymmetric Molecules," U.S. Clearinghouse, Fed. Sci. Tech. Inform., AD 1968, AD-682 838.

[6] See Ref. 3 and J. A. Lannon and E. R. Nixon, Spectrochim. Acta **23A,** 2713 (1967); A. B. Harvey and M. K. Wilson, J. Chem. Phys. **44,** 3535 (1966).

[7] M. T. Chen and J. W. George, J. Organometal. Chem. **12,** 401 (1968).

[8] C. W. Sink and A. B. Harvey, J. Mol. Structure **4,** 203 (1969).

[9] A. B. Harvey, F. E. Saalfeld, and C. W. Sink, Appl. Spectry. **24,** 466 (1970).

[10] J. R. Allkins and P. J. Hendra, Spectrochim. Acta **22,** 2075 (1966).

[11] J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules, V and VI," Tech. Rept. Nos. 231–264 and 57–65, respectively, Shell Development Co., Emeryville, Calif.

[12] J. H. Schachtschneider and R. G. Snyder, Spectrochim. Acta **19,** 117 (1963).

[13] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1958).