

Normal Coordinate Analysis of Methanol

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A normal coordinate analysis was performed for methanol. Harmonic force fields, potential energy distribution, and calculated mean amplitudes of vibration are reported. The results of mean amplitudes for CH₃OH agree well with previously given electron diffraction data.

Structural and spectral investigations have been conducted for many groups of organic molecules. Recently a systematic study of carboxylic acids by electron diffraction¹ and spectroscopic calculations² has been performed. The interest of the spectroscopic analyses was concentrated about mean amplitudes of vibration,³ which may be compared with observed values from electron diffraction. A similar study of alcohols would be of interest. In the present work a harmonic force field and calculated mean amplitudes for methanol, CH₃OH, are reported, as based on the most recent data of vibrational frequencies.⁴ Observed values of mean amplitudes for this molecule from electron diffraction are available.^{5,6}

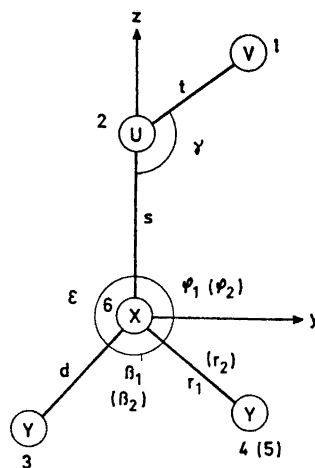


Fig. 1. The XY₂ZUV molecular model; symmetry C_s. The Y atoms number 4 and 5 are situated above and below the ZXUV plane, respectively. The employed valence coordinates are indicated except for τ , which is the ZXUV torsion.

Symmetry coordinates. Fig. 1 shows the appropriate XY_2ZUV model of C_s symmetry. The applied set of symmetry coordinates of molecular vibrations is given in the following.

Species A':

$$S_1 = 2^{-1/2}(r_1 + r_2), S_2 = d, S_3 = s, S_4 = t$$

$$S_5 = (RS/2)^{1/2}(\phi_1 + \phi_2), S_6 = (RD/2)^{1/2}(\beta_1 + \beta_2)$$

$$S_7 = (DS)^{1/2}e, S_8 = (ST)^{1/2}\gamma$$

Species A'':

$$S_1 = 2^{-1/2}(r_1 - r_2), S_2 = (RS/2)^{1/2}(\phi_1 - \phi_2)$$

$$S_3 = (RD/2)^{1/2}(\beta_1 - \beta_2), S_4 = (DT)^{1/2}\tau$$

Here the capital letters R , D , S , and T denote the equilibrium distances of $X - Y$, $X - Z$, $X - U$, and $U - V$, respectively.

Structural and spectral data. The present calculations are based on structural and spectral data from the compilations of Sverdlov *et al.*,⁴ with the slight modification that all interbond angles of the methyl group were assumed to be tetrahedral. The mentioned volume,⁴ which repeatedly has proved to be extremely useful, may be consulted for references to the original works. The experimental values of vibrational frequencies for four isotopic molecules of methanol in the gas phase are shown in Table 1.

Table 1. Calculated and observed vibrational frequencies (in cm^{-1}) for four isotopic molecules of methanol.

		CH ₃ OH		CH ₃ OD		CH ₃ OH		CH ₃ OD	
		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
A'	1	3687	3687	2973	2720	3687	3690	2688	2724
	2	2973	2973	2845	2965	2230	2235	2229	2228
	3	2845	2845	2688	2840	2079	2077	2079	2080
	4	1455	1455	1455	1458	1344	1134	1193	1135
	5	1425	1425	1419	1427	1168	(1061)	1095	1071
	6	1345	1345	1167	1210	1049	1297	1020	1029
	7	1070	1070	1034	1041	954	988	865	983
	8	1034	1034	912	865	771	858	770	775
A''	9	2973	2973	2973	2965	2219	2235	2219	2228
	10	1475	1475	1475	1475	1057	1081	1057	1083
	11	1160	1160	1160	1160	896	890	896	888
	12	270	270	214	(215)	256	(256)	197	(197)

Force field. A harmonic force field was developed by an iteration procedure through several steps using the experimental frequencies of CH₃OH and CD₃OD. The final set of force constants (see Table 2) are adjusted to fit exactly the observed frequencies⁴ of gaseous CH₃OH. Calculated frequencies for the four isotopic molecules in question are given in Table 1. For the present purpose they were judged to be in satisfactory agreement with the experimental values.

Table 2. Symmetry force constants (in mdyn/Å) for methanol.

1	4.756								Species A'
2	-0.032	4.575							
3	-0.022	-0.010	5.659						
4	0	-0.001	0.005	7.586					
5	0.008	0.016	0.160	0.005	0.870				
6	-0.005	-0.008	0.010	0.001	0.348	0.883			
7	0.010	0.005	0.132	0.002	0.091	0.340	0.841		
8	0.003	0.002	0.029	0	0.034	0.019	-0.005	0.611	
9	4.696								Species A''
10	0.003	0.560							
11	0	0.010	0.449						
12	0	0	0	0.0256					

Potential energy distribution. It is possible to give an approximate description of the normal modes on the basis of potential energy distribution. The present results for CH₃OH are shown in Table 3. The representations in parentheses (Table 3) accord with a modern way of describing the normal modes; see. *e.g.*

 Table 3. Approximate description of normal modes and potential energy distribution ^a for CH₃OH.

A'	1	O-H	stretching	(100t)
	2	C-H	stretching	(55r + 43d)
	3	C-H	stretching	(56d + 44r)
	4	HCH	bending	(83β + 55φ + 31ε + 21s)
	5	methyl	bending	(50ε + 43φ + 18γ)
	6	COH	bending	(64γ + 19β + 14ε)
	7	methyl bending/C-O	stretching	(37β + 27s + 14γ)
	8	C-O	stretching	(47s + 19φ + 15ε)
A''	9	C-H	stretching	(99r)
	10	HCH	rocking	(86β + 15φ)
	11	OCH	bending	(85φ + 13β)
	12	CO	torsion	(98τ)

^a P.E.D. terms smaller than 10 are omitted

Ref. 7. The present description is generally compatible with the version adopted by Sverdlov *et al.*; ⁴ one interesting detail may be mentioned namely that we have assigned ν_7 rather than ν_8 to C-O stretching.

Mean amplitudes of vibration. The calculated mean amplitudes of vibration (u) at absolute zero and 298°K are summarized in Table 4. The calculated values displayed no significant secondary isotope effect, the deviations being below 0.0001 Å in most cases. Hence it was possible to collect the results for all the four isotopic molecules in one table. The parenthesized values of equilibrium distances in Table 4 are calculated values from the structure parameters applied here.

Table 4. Mean amplitudes of vibration (\AA units) for isotopic molecules of methanol.

Distance type (<i>i-j</i>) ^a	(Equil. dist. in \AA)	<i>u</i> spectr.		<i>u</i> electr. diff. Ref. 6
		0	298°K	
O-H (1-2)	(0.960)	0.0695	0.0695	0.073 ± 0.015
O-D (1-2)	(0.960)	0.0592	0.0592	—
C-H (3-6)	(1.095)	0.0791	0.0791	0.080 ± 0.010
C-H (4-6)	(1.095)	0.0785	0.0785	
C-D (3-6)	(1.095)	0.0677	0.0677	—
C-D (4-6)	(1.095)	0.0672	0.0672	—
C-O (2-6)	(1.428)	0.0453	0.0455	0.049 ± 0.005
C...H (1-6)	(1.962)	0.1013	0.1015	0.110
C...D (1-6)	(1.962)	0.0875	0.0884	—
O...H (2-3)	(2.069)	0.1008	0.1011	0.099 ± 0.01
O...H (2-4)	(2.069)	0.1024	0.1027	
O...D (2-3)	(2.069)	0.0868	0.0875	—
O...D (2-4)	(2.069)	0.0882	0.0891	—
H...H (3-4)	(1.788)	0.1282	0.1284	0.140 (assumed)
H...H (4-5)	(1.788)	0.1368	0.1373	
H...H (1-3)	(2.862)	0.1221	0.1223	—
H...H (1-4)	(2.320)	0.1817	0.2059	—
H ₃ ...D ₁ (1-3)	(2.862)	0.1137	0.1140	—
H ₁ ...D ₃ (1-3)	(2.862)	0.1125	0.1129	—
H ₃ ...D ₁ (1-4)	(2.320)	0.1662	0.1968	—
H ₁ ...D ₄ (1-4)	(2.320)	0.1709	0.1978	—
D...D (3-4)	(1.788)	0.1081	0.1087	—
D...D (4-5)	(1.788)	0.1155	0.1171	—
D...D (1-3)	(2.862)	0.1033	0.1039	—
D...D (1-4)	(2.320)	0.1535	0.1883	—

^a According to the numbering of Fig. 1.

It is seen to be perfect agreement between the spectroscopic and electron diffraction values of mean amplitudes; cf. Table 4.

Added remark. After completion of this work another report on a normal coordinate analysis of methanol has appeared.⁸ No substantial contradictions with our results were found. The calculated mean amplitudes in our work are still an original contribution.

REFERENCES

- Almenningen, A., Bastiansen, O. and Motzfeldt, T. *Acta Chem. Scand.* **23** (1969) 2848; Náhlovská, Z., Náhlovský, B. and Strand, T. G. *Acta Chem. Scand.* **24** (1970) 2617; Derissen, J. L. *J. Mol. Struct.* **7** (1971) 67.
- Cyvin, S. J., Alfheim, I. and Hagen, G. *Acta Chem. Scand.* **24** (1970) 3038; Alfheim, I. and Cyvin, S. J. *Acta Chem. Scand.* **24** (1970) 3043; Cyvin, S. J. and Alfheim, I. *Acta Chem. Scand.* **24** (1970) 2648; Alfheim, I., Hagen, G. and Cyvin, S. J. *J. Mol. Struct.* *In press.*
- Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.
- Sverdlov, L. M., Kovner, M. A. and Krainov, E. P. *Kolebatelnye spektry mnogoatomnykh molekul* (Vibrational Spectra of Polyatomic Molecules). Izd. Nauka, Moscow 1970.
- Kimura, M., Kimura, K. and Shibata, S. *J. Chem. Phys.* **24** (1956) 622.
- Kimura, K. and Kubo, M. *J. Chem. Phys.* **30** (1959) 151.
- di Lauro, C., Califano, S. and Adembri, G. *J. Mol. Struct.* **2** (1968) 173.
- Timidei, A. and Zerbi, G. *Z. Naturforsch.* **25a** (1970) 1729.

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