Valence Force Constants and Normal Vibrations of Methanol *

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The possibility of reproducing the normal vibrations of methanol, CH_3OH, and its deutero-derivatives CH_3OD, CD_3OH, CD_3OD using a valence force field has been critically analyzed. A 13 parameter valence force field has been determined by least square calculations. The meaning of the obtained numbers and their validity in molecular spectroscopy are discussed and compared with the information already available in the literature. It is concluded that the vibrational modes of this molecule are fairly well known within the harmonic approximation.

The physical meaning of quadratic force constants derived from spectroscopic data is presently subject of a critical analysis by several authors. We feel that a discusion can be carried out only if data derived on a series of simple molecules with the use of the most recent computational techniques are available. In this paper we deal with methanol, whose spectrum has been already analyzed using both experiments [1] an calculations [2, 3].

Urey-Bradley [3] force field and a valence force field [2] (VFF) have been adopted for the understanding of the normal vibrations of this molecule. We believe, however, that the VFF previously derived suffers from a too large statistical degree of freedom. We wish therefore to determine by a least square process a VFF with a small number of well determined (i. e., small dispersion $\sigma\{\bar{\varphi}_i\}$) parameters.

For sake of consistency the experimental results by Margottin-Maclou [2] (MM) have been used in the present work. Close comparison with data reported by Falk and Whalley [1] reveals negligible differences in the location of absorption maxima for all but a few frequencies which will be discussed below. Recent tables of molecular vibrational frequencies published by Shimanouchi [4] list a set of frequencies which basically agree with those used in the present work. It is however well known that due to band overlapping it is difficult to locate absorption maxima for many of the fundamentals for low symmetry molecules.

The geometrical parameters from Ivash and Dennison [5] and Venkateswarlu and Gordy [6] (Fig. 1) have been adopted, exception made for the position of the oxygen which is taken on the C_3 axis of the methyl group. In view of the intrinsic approximations of a force constant calculation no real significance could be attached to possible differences in vibrational parameters obtained using the proper geometry. The structure of the irreducible representation for a C_s point group contains $8\,A'$ and $4\,A''$ normal modes. Both representations are infrared and Raman active. The factorization of the G and F matrices has been obtained by constructing a set of straightforward symmetry coordinates.

The starting set of valence force constants contained several interaction terms whose effectiveness in the least square fitting has been tested. After several attempts we have finally settled on a 13 parameter valence force field which is reported in Table 1 together with the corresponding dispersions. The choice of the starting values of the force constants has been guided by the attempt not to reach the same minimum in force constants space as that reached by MM. Several values have been taken from the VFF for ethers [7]. Satisfactory convergence

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Sym. class	i	ν_i	$\bar{\nu}_i$	e	PED
					CH_3OH
A′	1	3679	3696	−17	f_l (99); OH stretch.
	2	2960	2986	−26	f_d (99); CH deg. stretch.
	3	2883	2883	0	f_d (98); CH sym. stretch.
	4	1455	1471	−16	f_α (75); CH_3 deg. deform.
	5	1425	1431	−6	f_β (70), f_α (40); CH_3 sym. deform.
	6	1345	1344	1	f_γ (64); OH bend.
	7	1070	1071	−1	f_β (50), f_D (27), f_γ (28); CH_3 rock.
	8	1033	1045	−12	f_D (78); CO stretch.
A″	9	3000	2985	15	f_d (99); CH deg. stretch.
	10	1475	1468	7	f_α (82); CH_3 deg. deform.
	11	1160	1154	6	f_β (79); CH_3 rock.
	12	270	270	0	f_τ (99); C—O torsion
					CH_3OD
A′	1	2965	2986	−21	f_d (99)
	2	2885	2883	2	f_d (98)
	3	2716	2693	23	f_l (99)
	4	1458	1468	−10	f_α (81)
	5	1420	1431	−11	f_β (70), f_α (42)
	6	1210	1216	−6	f_β (57)
	7	1039	1054	−15	f_D (100)
	8	865	866	−1	f_γ (80)
A″	9	3000	2985	15	f_d (99)
	10	1475	1468	7	f_α (82)
	11	1160	1154	6	f_β (79)
	12	—	214	—	f_τ (99)
					CD_3OH
A′	1	3680	3696	−16	f_l (99)
	2	2215	2233	−18	f_d (97)
	3	2075	2076	−1	f_d (97)
	4	1297	1297	0	f_γ (89)
	5	1133	1121	12	f_D (54), $f_{D\beta}$ (39), f_β (54)
	6	—	1047	—	f_α (89)
	7	986	975	11	f_D (52)
	8	857	851	6	f_β (80)
A″	9	2260	2227	33	f_d (98)
	10	1031	1048	−17	f_α (87)
	11	890	895	−5	f_β (84)
	12	—	256	—	f_τ (99)
					CD_3OD
A′	1	2718	2693	25	f_l (99)
	2	2213	2232	−19	f_d (97)
	3	2074	2076	−2	f_d (97)
	4	1136	1123	13	f_D (59), $f_{D\beta}$ (38), f_β (49)
	5	1071	1060	11	f_γ (40), f_β (40)
	6	—	1044	—	f_α (87)
	7	981	962	19	f_D (45)
	8	775	772	3	f_γ (46), f_β (53)
A″	9	2260	2227	33	f_d (98)
	10	1083	1048	35	f_α (87)
	11	888	895	−7	f_β (84)
	12	—	196	—	f_τ (99)

Table 1. Observed (ν_i) and calculated ($\bar{\nu}_i$) frequencies, errors (e), in cm^{-1}, and potential energy distribution (PED) for methanol and deuterated derivatives from a 13 parameters valence force field.

has been reached after a few cycles with an average fitting of 0.74 percent. The final refinement has been carried out on 13 parameters.

Our usual criteria have been adopted in evaluating the reliability of force constants calculations within the presently accepted approximations: a) satisfactory frequency fit, b) use of the minimum set of force constants in order to reach a high ratio between observed data and adjustable parameters, c) reasonable force constants with small dispersions. Our calculations have fulfilled all the above criteria. Even if no general set of rules has been suggested to evaluate the acceptability of a given frequency fit, we feel that our results are below the commonly accepted level of error. The number of adjustable parameters determined in the present work is sensibly different from that given by MM. The slight differences between experimental values on which our calculations are based and those reported by SHIMANOUCHI [4] will not sensibly affect the values of the force constants obtained therefore changing the purpose of the present work. With the exception of f_{dd} and of $f_{\beta\gamma}$ the statistical dispersions of the force constants are low and show a reasonable stability of the least square refinement [8, 9]. The force constants values obtained for the mehtyl group of methanol follow a general pattern of force constants derived for the CH_3 group in chemically different molecules [7, 8, 10, 11].

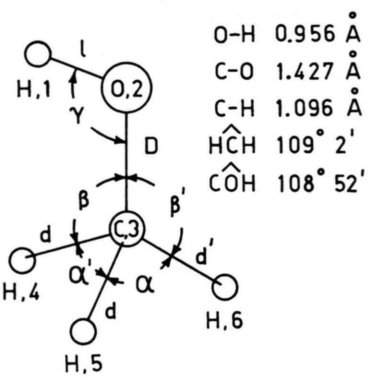

Fig. 1. Structure of methanol showing the definition of coordinates in the potential function.

In the light of what previously discussed we feel that our results are more meaningful than those by MM if any meaning can be attached to quadratic force constants.

The precise description of the motion of the atoms in each normal mode is derived in the present calculation from force constants as in Table 2. They are shown in Fig. 2 only for methanol and are described by the potential energy distribution for all isotopes in Table 1. It is pleasing to find that Shimanouchi's description is in nice agreement with the results of the present work. The molecular motions of methanol can then be considered fairly well known at least in the harmonic approximation.

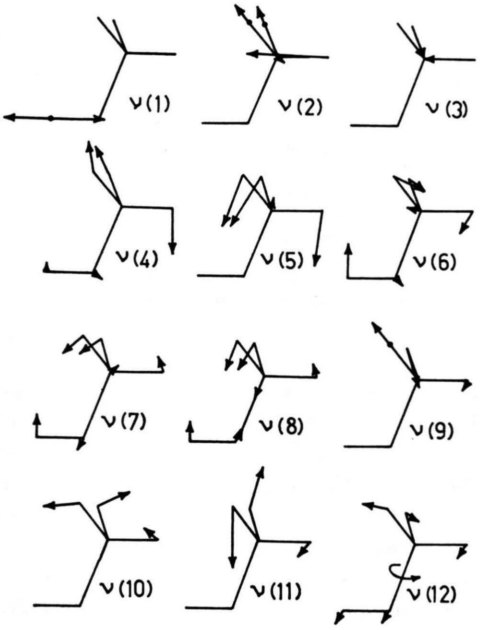

Fig. 2. Normal modes of vibration for methanol from a 13 parameters valence force field.

Force constant	Calculated value	$\sigma\{\bar{\varphi}_i\}$
f_l	7.623	0.041
f_D	5.221	0.117
$f_{D\gamma}$	0.246	0.072
$f_{D\beta}$	0.437	0.032
f_d	4.750	0.018
f_{dd}	0.019	0.013
f_γ	0.764	0.017
f_α	0.525	0.007
f_β	0.853	0.014
$f_{\beta\beta}$	−0.029	0.009
$f_{\beta\gamma}$	−0.013	0.035
$f_{\beta'\gamma}$	0.086	0.042
f_τ	0.008	—

Table 2. 13 parameters valence force field for methanol; f_l, f_D, f_d and f_{dd} are in units of 10^{-5} dynes/cm, f_D and f_D in 10^{-3} dynes/rad; the remaining parameters are in units of 10^{-11} dynes/rad^2. See Fig. 1 for definition of the internal coordinates.

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