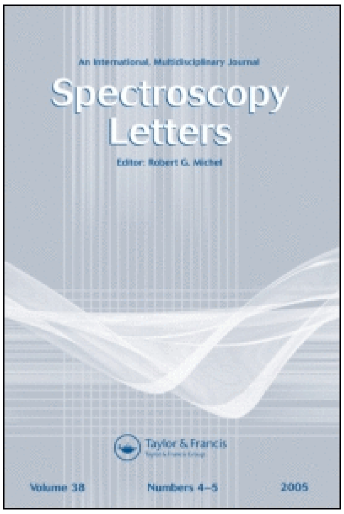

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Molecular Force Field of Methanol

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MOLECULAR FORCE FIELD OF METHANOL

Key Words: Normal coordinate analysis, Force field, Methanol

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ABSTRACT

Normal coordinate analysis was carried out on the vapor phase Raman and i.r. spectral data of methanol and its deuterated species to determine a vibrational force field. Based on the results of calculations, the 25-parameter molecular force field was analyzed and compared with the earlier studies and the vibrational band assignments were discussed in terms of the vibrational mode mixings, particularly, in the wavenumber region below 1500 cm^{-1}.

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INTRODUCTION

The force field of methanol and its isotopic species has been the subject of a considerable number of vibrational studies. The recent normal coordinate treatments[1-5] of free methanols were all performed using the i.r. data of the low temperature matrix isolated molecules instead of the vapor phase i.r. data because of its simplicity in observation aspects and, as a consequence, almost complete identification of fundamental bands. Mallinson and McKean[1] used a 29-parameter symmetry force field and analyzed the Fermi resonance shifts on the CH_3/CD_3 symmetric stretching fundamentals. Serrallach et al.[2] reported the vapor-matrix wavenumber shifts and determined a 15-parameter valence force field. Shortly, thereafter, Mallinson[3] used a 28-parameter symmetry force field to better reproduce the fundamental wavenumbers observed earlier[1,2,6]. Blom et al.[4] used a full 46-parameter general valence force field by scaled ab initio calculations. Brakaspathy and Singh[5] performed CNDO calculations to get an initial set of the bending and interaction force constants and the values were followed by the least squares refinement to obtain a 57-parameter valence force field.

Silva et al.[7] more recently reported the vapor phase Raman data of four isotopic methanols and showed that the observed Raman shifts were satisfactorily comparable with the vapor phase i.r. data. In the present study, a normal coordinate analysis is newly carried out to obtain the force constants for vapor phase methanols. The force field is discussed by comparison with the earlier studies.

MOLECULAR FORCE FIELD

A normal coordinate analysis was made for a staggered model of C_s molecular symmetry, shown in Fig. 1, and the structural

TABLE 1

Symmetry Coordinates

a':	$S_1 = \Delta t$		$\nu OH/\nu OD$
	$S_2 = (2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}$		$\nu_a CH_3/\nu_a CD_3$
	$S_3 = (\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}$		$\nu_s CH_3/\nu_s CD_3$
	$S_4 = (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)/\sqrt{6}$		$\delta_a CH_3/\delta_a CD_3$
	$S_5 = b(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3) - a(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)$		$\delta_s CH_3/\delta_s CD_3$
	$S_6 = \Delta\theta$		$\delta OH/\delta OD$
	$S_7 = (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6}$		$\rho CH_3/\rho CD_3$
	$S_8 = \Delta s$		νCO
a":	$S_9 = (\Delta r_2 - \Delta r_3)/\sqrt{2}$		$\nu_a CH_3/\nu_a CD_3$
	$S_{10} = (\Delta\alpha_2 - \Delta\alpha_3)/\sqrt{2}$		$\delta_a CH_3/\delta_a CD_3$
	$S_{11} = (\Delta\beta_2 - \Delta\beta_3)/\sqrt{2}$		$\rho CH_3/\rho CD_3$
	$S_{12} = \Delta\tau$		τCO

a = 0.4142363, b = 0.4021712.

parameters were from the millimeter wave study by Lees and Baker[8], rOH = 0.945 Å, rCO = 1.424 Å, rCH = 1.093 Å, <COH = $108^{\circ}32'$, <HCO = $110^{\circ}18'$ and <HCH = $108^{\circ}38'$, and the tilt angle was assumed to be equal to zero. The calculations were carried out by an application of the Wilson's GF matrix method[9,10].

The potential function of the force field was expressed in terms of the symmetry coordinates defined in Table 1, using the internal coordinates given in Fig. 1. The force field used in this study is analyzed by comparison with that of Serrallach, Meyer and Günthard[2] (SMG-FF, transferred to a symmetry force field[4]), Mallinson[3] (M-FF), and Blom, Otto and Altona[4] (BOA-FF, scaled ab initio calculations). The molecular force field by Brakaspathy and Singh[5] is not used for our purpose because many of the interaction force constants change drastically from the

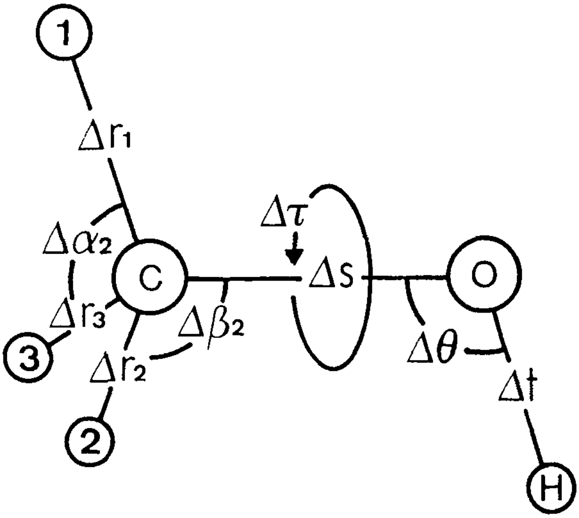

FIG. 1. Molecular structure and internal coordinates.

CNDO values to the refined ones. It is notes that the definitions of the CH_3/CD_3 symmetric bending coordinate are different in those studies. The symmetric F matrix, whose element $F_{i,j}$ is defined by the i-th and the j-th symmetry coordinate indices, is given as follows:

a'	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
S_1	$F_{1,1}$	(b)	(b)	(b)	(b)	(c)	(b)	(c)
S_2		$F_{2,2}$	(a)	$F_{2,4}$	(a)	(b)	$F_{2,7}$	(a)
S_3			$F_{3,3}$	(a)	$F_{3,5}$	(b)	(a)	(c)
S_4				$F_{4,4}$	(a)	(b)	$F_{4,7}$	(a)
S_5					$F_{5,5}$	$F_{5,6}$	(a)	$F_{5,8}$
S_6						$F_{6,6}$	$F_{6,7}$	$F_{6,8}$
S_7							$F_{7,7}$	(a)
S_8								$F_{8,8}$

a"	S_9	S_{10}	S_{11}	S_{12}
S_9	$F_{9,9}$	$F_{9,10}$	$F_{9,11}$	(d)
S_{10}		$F_{10,10}$	$F_{10,11}$	(d)
S_{11}			$F_{11,11}$	(d)
S_{12}				$F_{12,12}$

Of a total of the 36 a' symmetry potential parameters, the 9 elements denoted by (a) are, first, constrained to zero since for a C_{3v} local symmetry of the CH_3-O group those are the cross terms between the a_1 and the e symmetry coordinates. Indeed, the SMG-FF, M-FF and BOA-FF values are found in the range from 0.050 to -0.050 according with the respective units. However, three of M-FF ($F_{2,3}$ = 0.098 aJ.Å^{-2}, $F_{3,4}$ = 0.161 aJ.Å^{-1}, $F_{3,7}$ = 0.123 aJ.Å^{-1}) are not so close to zero; all are related with the CH_3/CD_3 symmetric stretching coordinate S_3.

The 8 elements denoted by (b), which are considered to be the less mechanically coupled terms regarding to the interactions between the OH/OD and CH_3/CD_3 group movements, are also expected to be small. This can be confirmed in SMG-FF, M-FF and BOA-FF. So, in our calculations, these (b)-type force constants are also constrained to zero.

The third group denoted by (c) in the F matrix consists of three terms and it is known, from preliminary exploration, to be difficult to determine its values simply by the least squares method. The BOA-FF values are $F_{1,6}$ = 0.169 aJ.Å^{-1}, $F_{1,8}$ = -0.034 aJ.Å^{-2}, $F_{3,8}$ = 0.268 aJ.Å^{-2}, and the M-FF value is $F_{3,8}$ = 0.098 aJ.Å^{-2}. Two other elements of M-FF and all three of SMG-FF were assumed to be zero. In this study, the value of $F_{1,8}$ is set to zero and $F_{3,8}$ is fixed to be 0.00, 0.10 or 0.27 aJ.Å^{-2} to analyze the influence of $F_{3,8}$ on the other force constants. For this condition, $F_{1,6}$ can be refined by the least squares method.

For the a" symmetry species, there are not (a)-, (b)- nor (c)-type parameters, but three cross terms involving the torsional coordinate S_{12}, denoted by (d), are constrained to zero. The BOA-FF values of $F_{9,12}$, $F_{10,12}$ and $F_{11,12}$ are from 0.023 to 0.006 according with the respective units. In the SMG-FF and M-FF calculations, all of those were set to zero.

The considerations taken above lead to a very similar force field to that of Mallinson and McKean[1] for methanol and are almost consistent to the General Group Force Field by Matsuura and Tasumi[11].

As a consequence, the 24 symmetry force constants, in which 23 are given as $F_{i.j}$ in the F matrix plus $F_{1,6}$, are determined for the vapor phase methanols. In accordance with the earlier studies[1,3], two hybrid orbital constraints $F_{2,4} = -F_{2,7}$ and $F_{9,10} = -F_{9,11}$ are imposed to make possible the least squares calculations.

RESULTS AND DISCUSSION

The symmetry force constants were adjusted to reproduce the 24 Raman and 46 i.r. fundamental wavenumbers observed for the four vapor phase isotopic methanols; CH_3OH, CH_3OD, CD_3OH and CD_3OD. By considering that the vapor-matrix band shifts reported are small, particularly in the low wavenumber region[2], some matrix isolation i.r. data were used to cover the lack of vapor phase fundamental wavenumbers.

As a weighting factor of the experimental wavenumbers in the force constant refinement, Serrallach et al.[2] and Blom et al.[4] used a constant factor, while Mallinson[3] considered it to be proportional to σ_{ν}^{-2}, where σ_{ν} are the observed wavenumbers. Because of the possible Fermi resonance shifts suggested on the CH_3 symmetric stretching vibrations, Mallinson did not include the relating fundamentals in the least squares procedure. Blom et al. also did not use the Fermi resonating fundamental bands to determine the scale factor on the ab initio force constants.

An anharmonicity correction on the observed wavenumbers is the another point to be considered. Serrallach et al.[2] and Blom et al.[4] employed the observed i.r. wavenumbers, without any anharmonicity corrections, in the force constant refinements. As a result, there were significant differences between the observed and calculated wavenumbers for the several fundamentals of the OH/OD and CH_3/CD_3 stretching vibrations. On the other hand, Mallinson[3] corrected the anharmonicity effects using Dennison's rule[12], with different correction factors, for the OH/OD stretching and bending, the CH_3/CD_3 stretching and bending, and the CO stretching bands, following the earlier study by Mallinson and McKean[1], and the calculations were carried out on the such harmonized wavenumbers.

In the present study, the force constant refinements are, in principle, performed for three cases depending upon the fixed values of $F_{3,8}$. A weighting factor of the observed fundamental wavenumbers is taken to be proportional to σ_{ν}^{-2} in the least squares procedures. The Fermi resonance effects of the CH_3/CD_3 symmetric stretching bands are not corrected on the wavenumbers because, in accordance to the recent Raman measurements[7], the effects are important to explain the observed intensities, but the calculated wavenumbers of overtones and combination bands indicate that in these cases those do not significantly affect the fundamental band positions. Although Dennison's rule[12] is useful to correct the anharmonicities on the fundamental bands, its application does not seem to be so convenient generally, when the fundamental vibrations are described as a mixture of the different types of vibrational modes. In methanol, as pointed out in the Raman study[7], the mode mixings are very important to understand the observed isotopic effects, particularly in the wavenumber region below 1500 cm^{-1}. Therefore, in this study, the anharmonicities are partially corrected only on the diagonal force constants relating to the OH/OD and CH_3/CD_3 stretching vibrations, using the empirical relation[13] of $F_{1,1}(D)/F_{1,1}(H) = F_{2,2}(D)/F_{2,2}(H) = F_{3,3}(D)/F_{3,3}(H) = F_{9,9}(D)/F_{9,9}(H) = 1.026$, and the observed wavenumbers are used without any corrections.

Three refined sets of the force constants are listed in Table 2 as Set 1 to Set 3, which correspond to $F_{3,8}$ = 0.00, 0.10 and 0.27 aJ.$Å^{-2}$, respectively, fixed in the calculations. Set 4 was obtained for comparison with the same conditions of Set 1 except for the use of a constant weighting factor for all observed Raman and i.r. spectral data. Also, Set 5 was obtained similarly to Set 1, but without anharmonicity corrections even on the force constants relating to the H/D substitution-sensitive vibrations. The mean differences between the 70 observed and calculated wavenumbers for the four isotopic methanols are 2.82, 2.81, 2.82, 2.34 and 6.98 cm^{-1}, respectively. As shown in Table 2, the force constants of Set 1 to Set 3 are almost independent upon the fixed values of $F_{3,8}$ except that the $F_{3,5}$ interaction parameter gives a marked change from -0.213 to -0.097 aJ.$Å^{-1}$. For $F_{5,6}$, the values of about 0.028 aJ indicate that this interaction parameter may be constrained to zero. A comparison of Set 1 and Set 4 points out that the use of two types of weighting factor, constant or proportional to σ_{ν}^{-2}, does not give significant changes in the calculated results. The observed and calculated wavenumbers in cm^{-1} using Set 1 are listed in Table 3 together with the P.E.D. (Potential Energy Distribution). Only the P.E.D. elements whose values are larger than 10 are given in Table 3.

An excellent fit to the observed wavenumbers using 25 of the full 46 parameters in the general valence force field indicates that the significant values of $F_{2,3}$, $F_{3,4}$ and $F_{3,7}$ in M-FF are due to the exclusion of the CH_3 symmetric stretching bands of

TABLE 2

Force Constants

	Set 1	Set 2	Set 3	Set 4	Set 5	
$F_{1,1}$	7.577	7.577	7.577	7.578	6.980	aJ.Å^{-2}
$F_{2,2}$	4.876	4.876	4.876	4.881	4.908	aJ.Å^{-2}
$F_{3,3}$	4.695	4.702	4.710	4.667	4.458	aJ.Å^{-2}
$F_{4,4}$	0.579	0.579	0.579	0.580	0.628	aJ
$F_{5,5}$	0.664	0.660	0.656	0.655	0.702	aJ
$F_{6,6}$	0.743	0.742	0.743	0.743	1.133	aJ
$F_{7,7}$	0.849	0.849	0.849	0.850	0.862	aJ
$F_{8,8}$	5.279	5.270	5.265	5.287	5.799	aJ.Å^{-2}
$F_{1,6}$	0.099	0.100	0.100	0.117	-1.508	aJ.Å^{-1}
$F_{2,4} = -F_{2,7}$	-0.217	-0.218	-0.218	-0.228	-0.203	aJ.Å^{-1}
$F_{3,5}$	-0.213	-0.170	-0.097	-0.105	0.372	aJ.Å^{-1}
$F_{3,8}$	0.00^*	0.10^*	0.27^*	0.00^*	0.00^*	aJ.Å^{-2}
$F_{4,7}$	-0.056	-0.056	-0.056	-0.056	-0.135	aJ
$F_{5,6}$	0.029	0.028	0.028	0.027	-0.014	aJ
$F_{5,8}$	0.571	0.562	0.553	0.552	0.853	aJ.Å^{-1}
$F_{6,7}$	0.076	0.076	0.076	0.076	0.096	aJ
$F_{6,8}$	0.414	0.414	0.413	0.416	0.381	aJ.Å^{-1}
$F_{9,9}$	4.851	4.851	4.851	4.818	4.848	aJ.Å^{-2}
$F_{10,10}$	0.598	0.598	0.598	0.584	0.575	aJ
$F_{11,11}$	0.854	0.854	0.854	0.839	0.835	aJ
$F_{12,12}$	0.026	0.026	0.026	0.026	0.026	aJ
$F_{9,10} = -F_{9,11}$	-0.439	-0.439	-0.439	-0.340	-0.257	aJ.Å^{-1}
$F_{10,11}$	-0.080	-0.080	-0.080	-0.071	-0.060	aJ

* Fixed values.

Set 1-3: Anharmonicity correction, Proportional weighting factor.

Set 4: Anharmonicity correction, Constant weighting factor.

Set 5: No anharmonicity correction, Proportional weighting factor.

TABLE 3

Wavenumbers and Potential Energy Distribution

		Raman[7]	I.r.[2]	Calc.	P.E.D. (using Set 1)
CH_3OH:	ν_1	3683.5	3681.5	3682.9	νOH 100
	ν_2	3000.2	2999.0	2999.6	$\nu_a CH_3$ 101
	ν_3	2847.5	2844.2	2849.6	$\nu_s CH_3$ 100
	ν_4		1478.4	1477.8	$\delta_a CH_3$ 97
	ν_5	1457.1	1454.5	1458.6	$\delta_s CH_3$ 109
	ν_6		1339.5	1344.7	δOH 62, ρCH_3 27
	ν_7	1071.8	1074.5	1074.7	ρCH_3 51, νCO 25, δOH 19
	ν_8	1033.5	1033.5	1033.1	νCO 87, δOH 25, ρCH_3 16
	ν_9		2970±4	2979.0	$\nu_a CH_3$ 100
	ν_{10}	1462.8	1465±3	1465.3	$\delta_a CH_3$ 102
	ν_{11}		1145±4	1146.4	ρCH_3 97
	ν_{12}		271.5*	272.2	τCO 100
CH_3OD:	ν_1	2716.5	2717.6	2717.6	νOD 100
	ν_2	3000.1	3001.0	2999.5	$\nu_a CH_3$ 101
	ν_3	2839.9	2840.8	2849.7	$\nu_s CH_3$ 100
	ν_4		1478.8	1477.6	$\delta_a CH_3$ 97
	ν_5	1455.0	1455.0	1458.4	$\delta_s CH_3$ 110
	ν_6	864.0	864.0	865.2	δOD 89, ρCH_3 21
	ν_7		1224.5	1219.2	ρCH_3 73, δOD 15
	ν_8	1038.5	1038.4	1042.5	νCO 111
	ν_9		2970±4	2979.0	$\nu_a CH_3$ 100
	ν_{10}	1462.7	1463±4	1465.3	$\delta_a CH_3$ 102
	ν_{11}		1142±3	1146.4	ρCH_3 97
	ν_{12}			215.7	τCO 100

TABLE 3

(continued)

		Raman[7]	I.r.[2]	Calc.	P.E.D. (using Set 1)
CD_3OH:	ν_1	3683.7	3682.5	3682.9	νOH 100
	ν_2		2242.0	2247.1	$\nu_a CD_3$ 102
	ν_3	2074.9	2073.5	2070.5	$\nu_s CD_3$ 100
	ν_4		1068.2*	1066.6	$\delta_a CD_3$ 99
	ν_5	1133.1	1129.7	1128.9	$\delta_s CD_3$ 94, νCO 46
	ν_6	1296.3	1295.8	1293.2	δOH 84
	ν_7		851.3	853.8	ρCD_3 92, δOH 14
	ν_8	985.0	984.5	983.3	νCO 66, $\delta_s CD_3$ 16
	ν_9		2212.4	2205.8	$\nu_a CD_3$ 104
	ν_{10}		1068.2*	1066.0	$\delta_a CD_3$ 107
	ν_{11}		897.5*	893.9	ρCD_3 104
	ν_{12}		259.0*	258.3	τCO 100
CD_3OD:	ν_1	2719.1	2717.4	2717.5	νOD 100
	ν_2		2250±2	2246.5	$\nu_a CD_3$ 102
	ν_3	2078.1	2074.0	2070.3	$\nu_s CD_3$ 100
	ν_4		1078±2	1081.2	$\delta_a CD_3$ 80, δOD 15
	ν_5	1139.5	1134.3	1134.6	$\delta_s CD_3$ 93, νCO 42
	ν_6	777.5	774.8	774.1	ρCD_3 59, δOD 51
	ν_7		1027.8	1030.4	δOD 39, ρCD_3 39, $\delta_a CD_3$ 19
	ν_8	981.8	980.0	978.1	νCO 61, $\delta_s CD_3$ 16
	ν_9		2212.6	2205.8	$\nu_a CD_3$ 104
	ν_{10}		1069.3	1066.0	$\delta_a CD_3$ 107
	ν_{11}		895.0*	893.9	ρCD_3 104
	ν_{12}			197.9	τCO 100

* Matrix isolation data.

CH_3OH and CH_3OD in the calculations because of Fermi resonance and also to the inclusion of these three force constants in the least squares refinement for the other isotopic methanols. As a partial correction of anharmonicity, a simple consideration that the diagonal symmetry force constants regarding the H/D substitution-dependent stretching vibrations may have different values with an empirical ratio of 1.026 is very useful to balance the observed spectral data of normal and deuterated methanols in the force constant refinement.

In the previous experimental study[7], two types of mode mixing were suggested in the vibrational assignments on the basis of the isotopic fundamental wavenumber shifts. One is between $\delta_s CH_3/\delta_s CD_3$ and νCO, and another is between $\delta OH/\delta OD$ and $\rho CH_3/\rho CD_3$. The calculations clearly show that the first mode mixing can be observed in P.E.D. for CD_3OH and CD_3OD giving ν_5 and ν_8, while for CH_3OH and CH_3OD the aspects in P.E.D. are quite different. As a result, it is found in CH_3OH and CH_3OD that the mixing is only kinematical and that in CD_3OH and CD_3OD it can be due to a combination of mechanical and kinematical couplings. For CH_3OH, νCO is further mixed with δOH and ρCH_3, mechanically. The second mixing of $\delta OH/\delta OD$ with $\rho CH_3/\rho CD_3$ is explained as due mainly to mechanical coupling and the variety of the mode mixing scheme among the four isotopic methanols is directly recognized from the P.E.D., which supports the discussion given in the Raman study[7]. The other fundamental vibrations of a' symmetry species and of all a" symmetry species are considered as the mechanically and kinematically free modes for the symmetry coordinates defined in Table 1.

CONCLUSIONS

Of the 46 parameters in the general valence force field of free methanol molecule, 25 parameters with two hybrid orbital constraints were determined for the vapor phase four isotopic methanols.

The excellent agreement between the observed and calculated wavenumbers shows that the 25-parameter force field in this study includes all important terms to describe the potential function of methanol molecule.

A simple anharmonicity correction using a relation on the diagonal force constants regarding the H/D substitution-sensitive stretching vibrations is useful in the calculations.

The vibrational mode mixings suggested experimentally from the isotopic fundamental wavenumber shifts were analyzed and explained in terms of the calculated P.E.D. elements.

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