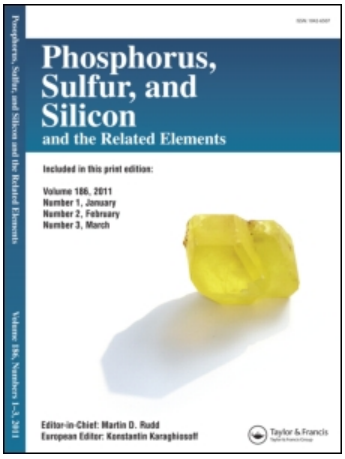

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CALCULATIONS OF THE STRUCTURE AND THE VIBRATIONAL INFRARED FREQUENCIES OF SOME METHYLPHOSPHONATES

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CALCULATIONS OF THE STRUCTURE AND THE VIBRATIONAL INFRARED FREQUENCIES OF SOME METHYLPHOSPHONATES

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We have calculated the energies, the optimized geometries and the vibrational infrared frequencies of methylphosphonic acid and three of its esters, namely the dimethyl ester, the diethyl ester and the diisopropyl ester. All computations are performed with the Gaussian 90 Program Package, utilizing both the 3-21G and the 6-31G* basis sets. We compare the computed vibrational frequencies and the corresponding IR and Raman intensities with the experimental data and we derive two different sets of correction factors that should be applied either to the 3-21G or to the 6-31G* computed frequencies.

Key words: Spectra; vibrational; infrared; Raman; methylphosphonates; methylphosphonic acid.

1. INTRODUCTION

Due to recent developments in computer technology it is possible to perform ab initio calculations of the electronic structures, equilibrium geometries, vibrational modes and frequencies and other physical properties of molecules of increasing size with ever improving accuracy. We are interested in calculating the geometries and the vibrational infrared frequencies of organic molecules and we have performed such calculations on groups of similar organic molecules by using one of the Gaussian Program Packages.[1] We found that the vibrational frequencies of organic molecules may be predicted with an accuracy of the order of 10%. The accuracy of the frequency predictions may be significantly improved by considering groups of similar molecules for which experimental IR or Raman data are available. By introducing empirical correction factors the accuracy of the frequency predictions may be improved to the order of 1%. We have analyzed a group of alcohols and ethers,[2] a group of mercaptans and sulfides[3] and a group of amines[4] and we have derived correction factors for these molecules that make it possible to predict the vibrational frequencies of similar molecules with improved accuracies.

In the present paper we report results of computations on a group of methyl phosphonic esters and of methyl phosphonic acid with the general formula $CH_3P(O)(OR)_2$. We had considered four different molecules: (1) methylphosphonic acid with R=H, (2) dimethylmethylphosphonate with R=CH_3=methyl,

(3) diethylmethylphosphonate with R=C_2H_5=ethyl, and diisopropylmethylphosphonate with R=$(CH_3)_2CH$=isopropyl. The structures of these four molecules exhibit some similarities, the four bonds P=O, P—CH_3, and the two P—OR bonds form a distorted tetrahedron around the phosphorus atom in every one of the four cases.

Our previous computations[2,3] were all based on the use of the 3-21G basis set. We pointed out that it is necessary to use a uniform basis set in all computations in order to derive consistent correction factors. In this paper we present two separate sets of computations, based on the use of the 3-21G basis sets and on the use of the 6-31G* basis sets, respectively. Consequently, we derive two different sets of correction factors, the first set is compatible with 3-21G computations and the second set is compatible with 6-31G* computations. All computations were performed on a Stardent 3000VS computer.

The Gaussian 90 Program Package[1] predicts the relative IR and Raman intensities of each vibrational mode and frequency. It is not quite clear how accurate these numerical predictions are but we find them quite helpful in deciding about vibrational assignments of the various IR and Raman lines. In order to save space we only list the IR intensities in our tables but we have also made use of the computed Raman intensities in making vibrational assignments. Our subsequent analysis is primarily based on IR absorption spectra but we make use of Raman spectral data in cases where experimental IR lines are not available.

2. RESULTS AND DISCUSSION

In order to predict the vibrational frequencies we have to derive first the optimized geometries of the various molecules. The four phosphorus bonds P=O, P—C and P—O—R (twice) form a slightly distorted tetrahedron. We derived the 3-21G and the 6-31G* optimized geometries of the four molecules, we do not list the detailed values of the corresponding bond lengths, bond angles and dihedral angles, those data are available upon request.

We organized a computer search of the literature on the structures and the spectra of the four molecules but we were unable to locate much information on the geometries. The only available information seems to be derived from measurements of the electric dipole moments. According to Kosolapoff[5] rotation of the O—R group can produce either extended or folded structures. Kosolapoff concluded that the extended structures are more consistent with his analysis of the electric dipole values than the other alternative. It should be noted that a similar analysis by Katolichenko[6] et al. leads to a different conclusion. Our computations seem to be in agreement with Kosolapoff rather than Katolichenko et al.

Our computations show that the bond lengths and the bond angles in the center parts are very similar for the four molecules we studied. We noted that an increase in the size of the alkyl group (from hydrogen to isopropyl) is accompanied by increases in the P=O and P—CH_3 bond lengths, on the other hand, the P—OR bond length in the isopropyl ester is slightly smaller than in the acid. In general it may be concluded that the differences in bond lengths and bond angles in the four molecules are minor. The variations in bond lengths are of the order of 0.01 angstroms and the variations in bond angles are of the order of 1 degrees, these

variations are comparable with the experimental errors in X ray structure determinations.

We found that the 6-31G* geometry parameters are also very similar for the four molecules we have studied but they are quite different from the corresponding 3-21G values. It is our experience that the introduction of polarization functions improves the accuracy of the bond lengths involving the phosphorus atom by a considerable margin. We found that the 6-31G* values for the P=O bond lengths are about 0.06 angstroms shorter than the 3-21G values. The 6-31G* P—O bond lengths are 0.045 angstroms shorter than the 3-21G values. All other bond lengths and bond angles are fairly similar in the two different computations, 6-31G* and 3-21G. Even the dihedral angles are comparable in both cases.

In the 3-21G computations we varied all C—H bonds lengths and all H—C—H bond angles independently but in the 6-31G* computations we required some of the C—H bond lengths to be equal to each other in the diisopropyl ester. We felt that this restriction did not make all that much difference and it was helpful in limiting the computational effort.

The vibrational infrared and Raman spectra of a group of dialkyl hydrogen phosphites, dialkyl methylphosphonates and of dialkyl ethyl phosphonates were reported as early as 1950 by Meyrick and Thompson.[7] They measured both the infrared and the Raman spectra of three of the molecules that we have studied theoretically, namely the three esters. Maarsen, Smit and Matze[8] reported the Raman and infrared spectra of a group of molecules with the general formula $(iH_7C_3O)_2PXO$, this group contains the molecule diisopropyl methylphosphonate, which is of interest to us. Subsequently Gerding, Maarsen and Zijp[9] measured the vibrational spectra of the methylphosphonate ion. Some authors concentrated their efforts on certain specific lines in the spectra only. For instance, Herail[10,11] paid particular attention to the CH_3—P and CH_3—OP vibrational modes, in a later effort the same author[12] concentrated on the P=O mode. We should also mention the work by Guilbault et al.[13] and by Quinchon et al.[14]

Van der Veken and Herman[15] presented a very careful and very elaborate experimental study of the spectrum of dimethyl methylphosphonate. They measured both the infrared and the Raman spectra of the standard molecule and of various deuterium and ^{13}C substituted species. The authors also reviewed previous experimental work on dimethyl methylphosphonate. On the basis of all available information they presented a complete assignment of all vibrational modes of the molecule. We use their results as a basis for analyzing our computational data of the dimethyl ester.

It is unfortunate that experimental studies accompanied by such a thorough and extensive analysis are not available for the other molecules that we have studied. Recently, the IR absorption spectra of methylphosphonic acid and of its dimethyl and diisopropyl esters have been measured in our laboratory by Piffath.[16] We use these experimental results for an analysis of our computations on methylphosphonic acid and its diisopropyl ester. In the case of the diethyl ester we base our analysis on the experimental work of Meyrick and Thompson.[7]

We begin our analysis of the theoretical results with the smallest of the four molecules, methylphosphonic acid. We decide on the assignments of the vibrational modes by studying the motions of the nuclei for each vibrational mode. The most

prominent lines involve the P=O stretch mode and the two P—O stretch modes. In these cases the nuclear motion is clearly localized to the bonds involved and the vibrational assignments are obvious and unambiguous. The same is true for the P—C stretch mode. The molecule has two O—H bonds and there are two O—H stretch modes and two O—H bend modes that are easily identified. We also recognize three C—H stretch modes of the three C—H bonds in the methyl group attached to the phosphorus atom. This methyl group is also involved in a rocking motion of the entire group, this rocking motion corresponds to two different vibrational modes. In the methyl group there are also three H—C—H bending modes. We denote these by PC—H bend in order to differentiate them from other C—H—C bending modes in the other molecules. Finally there is a rocking mode involving the three oxygens attached to the phosphorus and two wagging modes of the P=O and the P—O—H groups at relatively low frequencies.

Piffath[16] measured the infrared absorption spectrum of solid methylphosphonic acid. Gerding, Maarsen and Zijp[9] measured both the Raman and the infrared spectra for solutions in water and in acetone. The latter authors believe that the aqueous solution contains the methylphosphonate ion. Thus is consistent with our observation that the O—H stretch frequencies seem to be missing in their reported spectra data. There seem to be some more differences between the spectra reported by Piffath[16] and those reported by Gerding et al.[9] We decided to take Piffath's experimental data as the basis for our analysis.

We list both the 3-21G and the 6-31G* computed vibrational frequencies of methylphosphonic acid in Table I, together with the corresponding experimental

TABLE I

Vibrational frequencies of methylphosphonic acid. In the first column we list the type of vibrational mode, in the second column the corresponding experimental frequency, in the subsequent two columns we list the 3-21G computed frequencies and their relative intensities and in the last two columns we list the same information for the 6-31G* computations

mode	exp[16]	3-21G	int	6-31G*	int
CPO_3 wag	407.1	428.8	79.8	411.0	9.1
$O_2P{=}O$ bend	458.1	444.1	179.0	465.7	122.6
$O_2P{=}O$ bend	495.7	446.6	165.8	477.0	99.1
P-C str	767.7	783.0	9.5	789.5	13.2
P-O str	933.6	923.1	171.5	938.1	148.0
P-O str	953.9	954.9	289.3	960.1	175.0
$P\text{-}CH_3$ rock	?	1057.0	32.2	1017.0	90.5
$P\text{-}CH_3$ rock	1010.8	1072.0	75.0	1054.2	258.3
O-H bend	1114.9	1119.3	96.7	1106.0	73.1
O-H bend	1154.5	1119.8	75.5	1156.2	64.9
P=O str	1323.3	1287.1	216.3	1405.6	133.2
PC-H bend	1422.6	1547.1	49.6	1516.9	49.2
PC-H bend	1534.5	1620.2	17.8	1600.7	5.7
PC-H bend	1534.5	1620.6	13.3	1601.4	2.8
$PC\text{-}H_3$ str	2932.0	3240.8	0.1	3231.6	0.8
$PC\text{-}H_3$ str	3012.0	3326.0	0.2	3317.0	3.9
$PC\text{-}H_3$ str	3012.0	3326.7	0.1	3318.5	4.4
O-H str	3819.0	3912.2	107.4	4078.8	150.4
O-H str	3887.0	3916.8	146.7	4083.2	208.2

frequencies reported by Piffath.[16] We match the experimental IR absorption frequencies with the computed vibrational frequencies by considering the location of the lines and their intensities. Subsequently we make sure that the assignments are consistent with the other molecules. The assignments in Table I are fairly straightforward since the molecule is relatively small. We list both the 3-21G and the 6-31G* results. The two sets of frequencies are fairly similar except for the P=O stretch frequencies. It should be noted that the P=O bond lengths are also quite different for the different basis sets and it is therefore not surprising that the stretch frequencies differ by as much as 130 wave numbers. In Table I we also list the computed IR absorption intensities, they offer useful guidelines for the assignments. Due to lack of space we do not list the Raman intensities even though those values were also computed.

The major IR lines that are characteristic for the methylphosphonic acid molecule are the P=O stretch, the two P—O stretches, the two O—H stretches and the CH_3 rock. The other lines have lower intensities or they are not characteristic for the molecule. We shall see that the characteristic lines for the three esters are somewhat different than those for the acid.

We base our analysis of our computed vibrational spectra of dimethyl methylphosphonate on a comparison with the work of Van der Veken and Herman.[15] We derived spectral assignments by analyzing the nuclear motion in each vibrational mode. We report the experimental and the two sets of computed frequencies in Table II. The dominant IR and Raman lines in the esters correspond to a composite of P—O and O—C stretch modes involving the whole C—O—P—O—C skeleton. The other dominant line is the P=O stretch mode. There are of course many other vibrational modes. One type involves a rocking motion of the CH_3 group. This mode produces six frequencies, two of them belong to the methyl group attached to the phosphorus and the other four belong to the two methyl groups attached to the oxygens. Another type of vibrational mode corresponds to the P—C stretch and yet another type gives two O—P—O bending modes. Finally, we have a large number of C—H stretch modes and a large number of H—C—H bend modes. In both cases we differentiate between those modes that are localized on the P—CH_3 group and those that are localized on one of the O—CH_3 groups, but otherwise we list them as groups.

It may be seen in Table II that the P=O stretch frequency is again affected the most by the change in basis set, the difference is 124 wave numbers. In all other cases the differences are relatively small. It should be noted though that the assignments of some of the C—H stretch frequencies are reversed in the two computations, in the 6-31G* computation we assign the pair of PC—H stretch frequencies to 2951 wave numbers and in the 3-21G computation we assign them to 2992 wave numbers. Even though the differences between the two sets of computed frequencies are small we believe that the 6-31G* results are more consistent than the 3-21G results, they show smaller variations in the ratios. The 6-31G* computations should therefore be considered more reliable.

We mentioned already that our analysis of diethyl methylphosphonate is based on the experimental work of Meyrick and Thompson,[7] these are the only experimental data available for this molecule. It should be noted that the data on other molecules that are reported by Meyrick and Thompson show excellent agreement

TABLE II

Vibrational frequencies of dimethyl methylphosphonate. Definitions are identical with Table I

mode	exp[15]	3-21G	int	6-31G*	int
CPO_3 wag	398	407.1	53.3	422.8	31.9
$O_2P{=}O$ bend	468	482.4	29.2	520.3	26.1
CPO_3 wag	500	513.6	58.2	547.6	44.2
O-P-O bend	712	738.4	24.8	775.8	31.6
O-P-O bend	786	857.7	43.5	859.4	95.7
P-C str	818	885.6	68.5	881.1	86.5
$P\text{-}CH_3$ rock	894	1052.4	43.7	1014.4	48.0
$P\text{-}CH_3$ rock	912	1087.0	93.2	1033.5	170.5
COPOC str	1037	1175.1	347.5	1178.7	364.5
COPOC str	1064	1190.3	360.9	1218.1	407.0
$O\text{-}CH_3$ rock	1152	1265.2	5.5	1295.2	3.0
$O\text{-}CH_3$ rock	1152	1268.4	14.4	1296.8	2.9
O-C stretch	1183	1301.4	48.9	1324.4	45.1
O-C stretch	1183	1303.0	62.4	1324.8	26.2
P=O str	1250	1256.3	96.4	1380.1	237.1
PC-H bend	1308	1541.6	46.9	1513.7	45.9
PC-H bend	1418	1618.2	5.4	1602.2	4.8
PC-H bend	1418	1621.6	10.6	1602.3	4.2
H-C-H bend	?	1619.7	8.5	1627.9	0.1
H-C-H bend	?	1625.9	6.1	1634.4	4.9
H-C-H bend	1450	1677.0	2.0	1649.1	6.2
H-C-H bend	1463	1681.0	12.0	1654.5	2.2
H-C-H bend	1463	1686.0	10.7	1655.7	5.1
H-C-H bend	1463	1689.4	0.9	1659.2	5.0
$OC\text{-}H_3$ str	2848	3220.5	10.1	3236.2	12.4
$OC\text{-}H_3$ str	2848	3222.8	59.4	3240.0	87.0
$PC\text{-}H_3$ str	2848	3239.6	0.1	3231.7	1.5
$OC\text{-}H_3$ str	2951	3290.5	31.8	3316.8	67.2
$OC\text{-}H_3$ str	2951	3291.9	31.7	3319.5	18.2
$OC\text{-}H_3$ str	2992	3323.4	32.9	3347.9	11.5
$OC\text{-}H_3$ str	2992	3324.2	6.4	3348.4	28.7
$PC\text{-}H_3$ str	2951	3324.8	0.2	3315.7	3.9
$PC\text{-}H_3$ str	2951	3326.0	0.2	3318.9	18.2

with other sources. We list the experimental frequencies for the diethyl ester together with both sets of 3-21G and of 6-31G* computed frequencies in Table III, we use the same format as in the previous tables. The main features of the diethyl ester spectrum are quite similar to the main features of the dimethyl ester spectrum. We can again identify the P=O stretch mode, the two C—O—P—O—C stretch modes, the P—C stretch and the two P—CH_3 rocking modes. Obviously, the diethyl ester has a number of additional vibrational modes relative to the dimethyl ester. For instance, we now have two C—C stretch modes and we also have two CH_2 rocking modes in addition to the four C—CH_3 and the two P—CH_3 rocking modes. We also have a few more C—H stretch modes, now we have three groups, belonging to the CH_2, the C—CH_3 and to the P—CH_3 groups respectively. We also have some additional H—C—H bending modes. It should finally be noted that the present vibrational assignments are greatly facilitated by the available information on the dimethyl ester.

Finally we consider the diisopropyl ester of methylphosphonic acid. Here our analysis is based on the experimental work by Piffath.[16] The experimental frequencies together with the 3-21G and the 6-31G* computed results are presented in Table IV. The format is identical with the other tables. The most important

TABLE III

Vibrational frequencies of diethyl methylphosphonate. See Table I for definitions

mode	exp[7]	3-21G	int	6-31G*	int
O-P-O bend	?	451.1	22.5	456.3	12.0
CPO_3 wag	485	501.8	32.3	541.6	52.2
$O_2P{=}O$ bend	502	508.9	68.1	544.2	37.0
O-P-O bend	715	759.9	24.2	806.4	30.8
O-P-O bend	771	835.6	23.6	849.9	48.3
P-C str	806	863.2	43.6	864.8	59.4
CH_3 rock	?	912.0	0.1	883.6	0.6
CH_3 rock	?	913.4	3.6	885.6	0.6
$P\text{-}CH_3$ rock	898	1051.6	49.7	1012.6	17.4
$P\text{-}CH_3$ rock	939	1088.6	112.7	1020.7	17.4
C-C str	965	1025.5	5.9	1045.7	80.9
C-C str	965	1027.3	26.4	1051.1	344.6
COPOC str	1023	1173.6	564.1	1170.2	453.6
COPOC str	1049	1174.8	219.6	1199.3	233.8
O-C str	?	1225.8	17.3	1223.5	0.0
O-C str	1099	1235.2	164.9	1232.4	168.5
CH_3 rock	?	1293.5	3.8	1296.7	0.1
CH_3 rock	1164	1295.6	55.1	1297.9	8.2
P=O str	1250	1264.3	100.4	1379.3	241.9
CH_2 rock	?	1434.7	0.1	1431.6	0.2
CH_2 rock	?	1437.8	0.4	1436.1	0.7
PC-H bend	1314	1540.1	55.5	1513.0	45.9
H-C-H bend	?	1540.9	14.0	1540.9	4.6
H-C-H bend	?	1545.7	1.6	1544.3	7.0
H-C-H bend	?	1575.6	17.0	1579.8	31.1
H-C-H bend	?	1575.9	1.9	1583.3	9.7
PC-H bend	1390	1620.4	14.9	1602.7	5.2
PC-H bend	1390	1621.1	13.6	1602.9	4.4
H-C-H bend	1420	1655.6	0.7	1628.1	1.4
H-C-H bend	1420	1655.7	11.0	1628.3	6.5
H-C-H bend	?	1672.6	0.0	1643.9	0.4
H-C-H bend	1445	1673.0	7.7	1644.5	2.0
H-C-H bend	1480	1695.5	2.8	1676.5	0.8
H-C-H bend	1480	1698.3	1.0	1680.2	0.6
$CC\text{-}H_3$ str	2863	3214.5	32.2	3214.8	42.6
$CC\text{-}H_3$ str	2863	3214.7	1.2	3215.1	7.3
$CC\text{-}H_3$ str	2935	3281.5	1.8	3281.5	6.0
$CC\text{-}H_3$ str	2935	3281.7	58.7	3281.6	23.3
$CC\text{-}H_3$ str	2943	3297.5	8.6	3286.1	0.4
$CC\text{-}H_3$ str	2943	3298.4	57.3	3286.5	91.6
$C\text{-}H_2$ str	2885	3229.1	4.2	3233.5	7.1
$C\text{-}H_2$ str	2885	3232.3	0.1	3239.4	57.8
$C\text{-}H_2$ str	2990	3271.7	0.0	3315.3	20.0
$C\text{-}H_2$ str	2990	3272.1	2.1	3316.7	49.6
$PC\text{-}H_3$ str	2880	3239.2	0.1	3231.3	1.7
$PC\text{-}H_3$ str	2990	3324.0	0.3	3314.9	4.9
$PC\text{-}H_3$ str	2995	3325.5	0.2	3318.3	14.3

vibrational frequencies of the diisopropyl esters are similar to the smaller molecules and a comparison between the three esters makes the frequency assignments a task of manageable proportions. Nevertheless, the isopropyl ester has many more additional vibrational modes than even the diethyl ether. For instance, in the present case we have C—C and C—O stretch modes and C—C—C bend modes. The number of C—H stretch modes and of H—C—H bend modes is quite large and it is increasingly difficult to differentiate between the various modes within one group.

TABLE IV

Vibrational frequencies of diisopropyl methylphosphonate. See Table I for definitions

mode	exp[8,16]	3-21G	int	6-31G*	int
CH_3 wag	451	504.5	19.5	521.7	12.6
CPO_3 wag	504	523.4	64.4	541.8	48.3
$O_2P{=}O$ bend	541	539.5	42.4	562.1	43.4
O-P-O bend	719	749.6	29.2	794.4	26.8
O-P-O bend	748	798.0	4.4	819.9	15.6
P-C str	791	839.1	39.2	852.1	53.3
C-C-C bend	884	935.4	28.7	956.6	20.4
C-C-C bend	884	939.6	8.1	957.8	23.7
P-CH_3 rock	899	1045.8	42.5	1014.2	36.5
CH_3 rock	?	1032.0	2.2	1019.7	2.4
CH_3 rock	?	1032.4	1.2	1022.2	3.0
P-CH_3 rock	917	1078.5	40.0	1027.1	118.5
C-H bend	938	1057.9	3.6	1030.6	10.7
C-H bend	938	1060.8	2.6	1031.9	39.8
COPOC str	994	1145.1	284.6	1110.4	709.6
COPOC str	1018	1150.8	591.6	1139.9	279.4
O-C_3 str	1110	1235.6	32.3	1249.0	310.0
O-C_3 str	1115	1271.4	110.8	1253.4	53.4
C-C str	1115	1247.9	6.0	1255.8	16.5
C-C str	1115	1260.7	90.8	1260.1	46.4
C-C str	1177	1326.9	35.8	1312.8	26.6
C-C str	1183	1330.4	32.3	1316.4	15.3
P=O str	1251	1264.8	106.6	1377.8	227.1
C-H bend	1350	1502.1	16.8	1498.7	6.3
PC-H bend	1362	1537.8	48.6	1511.1	44.9
C-H bend	?	1503.0	20.3	1516.3	0.9
C-H bend	1385	1515.6	14.0	1530.2	20.6
C-H bend	1390	1518.4	23.0	1537.1	15.6
H-C-H bend	?	1565.4	11.7	1564.1	8.7
H-C-H bend	?	1568.6	12.7	1567.8	14.9
H-C-H bend	?	1581.8	19.6	1575.1	22.4
H-C-H bend	?	1585.8	22.4	1577.1	18.6
PC-H bend	1419	1619.5	13.2	1601.6	4.3
PC-H bend	1419	1622.1	14.2	1604.4	4.2
H-C-H bend	?	1651.9	1.5	1626.8	0.5
H-C-H bend	?	1652.7	4.4	1627.5	0.5
H-C-H bend	?	1658.7	3.7	1630.7	0.0
H-C-H bend	?	1660.8	3.8	1633.2	0.5
H-C-H bend	1453	1666.5	0.9	1638.2	1.8
H-C-H bend	1453	1667.2	0.6	1639.5	4.6
H-C-H bend	1475	1690.2	10.9	1652.3	4.0
H-C-H bend	1475	1690.5	18.1	1656.4	5.4
CC-H_3 str	?	3208.8	10.6	3208.9	25.9
CC-H_3 str	?	3209.1	13.8	3209.8	20.0
CC-H_3 str	2872	3213.7	10.8	3214.9	13.4
CC-H_3 str	2872	3213.9	22.2	3215.7	19.3
PC-H_3 str	2886	3236.6	0.2	3229.7	1.9
C-H str	2902	3245.3	9.7	3256.0	4.2
C-H str	2913	3249.7	3.0	3268.3	7.7
CC-H_3 str	2921	3273.8	0.7	3276.9	1.1
CC-H_3 str	2921	3274.5	0.4	3277.9	1.1
CC-H_3 str	2921	3279.5	27.4	3280.2	21.4
CC-H_3 str	2943	3280.1	27.7	3282.7	46.2
CC-H_3 str	2945	3285.2	29.7	3284.0	56.2
CC-H_3 str	2945	3286.5	25.5	3288.0	39.4
CC-H_3 str	2963	3291.0	49.3	3293.8	63.7
CC-H_3 str	2963	3292.8	26.4	3298.1	68.0
PC-H_3 str	2986	3318.9	0.6	3312.9	8.7
PC-H_3 str	2986	3325.2	0.3	3315.4	6.2

It may be seen from the tables that there is a remarkable similarity between the three different esters if we look at one particular vibrational mode, this is true both for the computed and for the experimental frequencies. In previous work we used the 3-21G basis set consistently for all frequency computations and we found that the results were satisfactory if we introduced correction factors. Now that we have improved computer capability we decided to extend the calculations to the use of the 6-31G* basis set. We believe now that the use of the larger basis set is preferable. It is not so much that the computed frequencies are more accurate (the errors are still of the order of 10%), but the results are more consistent so that the introduction of correction factors becomes more consistent.

3. CORRECTION FACTORS

An inspection of the data in Tables I to IV shows that the differences between the experimental values and either the 3-21G or the 6-31G* computed results are of the order of 10%. It is generally believed that this is typical of the differences between computed and experimental frequencies.

The degree of accuracy for predicting vibrational frequencies from computed results may be improved by introducing empirical correction factors.[17] A possible approach is the scaling of the molecular force constants, for instance Pulay and Meyer[18,19] suggested a uniform scaling factor of 0.9 for all diagonal stretching force constants and a factor 0.8 for the bending constants. Alternative schemes for scaling force constants were proposed by Blom et al.[20,21] and by Bock et al.[22,23]

In previous work[2-4] we have expressed a preference for scaling the frequencies themselves rather than the force constants. This approach is much simpler than scaling the force constants. In addition we believe that it can lead to more accurate frequency predictions, in particular if we introduce different scaling factors for different vibrational modes. The theoretical procedure for computing frequencies contains some approximations that are not always valid, the most obvious one is the harmonic approximation. It should also be noted that the experimental frequencies may depend on effects that are not even considered in the theory such as Fermi resonance, solvent shifts, molecular interactions, etc. All these effects are automatically accounted for if we introduce empirical correction factors for each frequency mode.

We have calculated the ratio of each experimental Raman or IR absorption frequency and the corresponding theoretical frequency, both for the 3-21G and for the 6-31G* computations. In order to derive the empirical frequency correction factors we average those ratios for all available frequencies belonging to the same vibrational mode for the three esters. In proposing this procedure we assume that the ratios within each group are within a narrow range. We found that this condition is generally satisfied for the three esters, here the variation of the ratios within each group is of the order of 1% or sometimes even less. The condition is not met if we include methylphosphonic acid, this molecule has a structure that is different from its esters and the few ratios that are compatible with the esters are significantly different. We decided therefore to derive the frequency correction factors by considering the spectra of the three esters only and to exclude methylphosphonic acid from the averaging process. The values of the frequency correction factors that

TABLE V
Correction factors for 3-21G and for 6-31G* computed frequencies

mode	corr 3-21G	corr 6-31G*
COPOC stretch	0.882	0.883
P=O stretch	0.991	0.901
P-C stretch	0.944	0.930
C-H stretch	0.895	0.893
O-C stretch	0.896	0.891
C-C stretch	0.915	0.907
P-CH_3 rock	0.852	0.892
C-H bend	0.915	0.884
O-P-O bend	0.937	0.907
O_2P=O bend	0.987	0.928
C-PO_3 wag	0.969	0.922

were obtained in this way are listed in Table V, the values in the first column are applicable to 3-21G frequency computations and the values in the second column should be used for 6-31G* computations.

4. CONCLUSIONS

It is interesting to compare the two sets of correction factors in Table V. The variation in the group of 6-31G* factors is significantly smaller than the corresponding variation in the group of 3-21G factors. The difference between the largest and the smallest correction factors in the 6-31G* group is 5% and the same difference for the 3-21G gropu is 12%. The most notable difference occurs for the P=O stretch frequency where the correction factor is 0.99 in the 3-21G case and 0.90 in the 6-31G* case.

In previous work[2,3] we have argued that the use of the 3-21G basis set produces frequency predictions with an accuracy of the order of 1% as long as different correction factors are applied to each vibrational mode. We see no reason to revise this opinion. On the other hand, the correction factors for the 6-31G* computations seem to be more consistent than in the other case and this gives us more confidence about the accuracy of the 6-31G* predictions. Also, if we introduce a general average correction factor for all 6-31G* computed frequencies the accuracy of the corresponding frequencies should be no worse than 2%. It should then be possible to make 6-31G* frequency predictions in situations where little experimental information is available.

Because of the above added features we believe that the use of the 6-31G* basis set is preferable to the use of the 3-21G basis set in making frequency predictions. It is possible that the use of the 6-311G** basis set is better yet but the use of the latter basis set for large molecules is still beyond our present computing facilities.

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