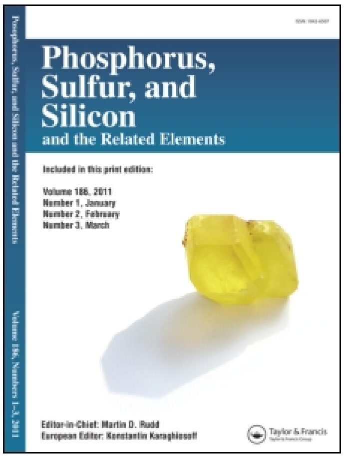


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

INFRARED SPECTRA OF TWO ISOTOPOMERS OF ISOPROPYLPHOSPHINE: A THEORETICAL STUDY

Daniel Zeroka[a]; James O. Jensen[a]
[a] Edgewood Research, Development, and Engineering Center Aberdeen Proving Ground, MD

To cite this Article Zeroka, Daniel and Jensen, James O.(1998) 'INFRARED SPECTRA OF TWO ISOTOPOMERS OF ISOPROPYLPHOSPHINE: A THEORETICAL STUDY', Phosphorus, Sulfur, and Silicon and the Related Elements, 141: 1, 201 — 220

To link to this Article: DOI: 10.1080/10426509808033733

URL: http://dx.doi.org/10.1080/10426509808033733

Phosphorus, Sulfur and Silicon, 1998, Vol. 141, pp. 201-220
Reprints available directly from the publisher
Photocopying permitted by license only

INFRARED SPECTRA OF TWO ISOTOPOMERS OF ISOPROPYLPHOSPHINE: A THEORETICAL STUDY

DANIEL ZEROKA*† and JAMES O. JENSEN

Edgewood Research, Development, and Engineering Center Aberdeen Proving Ground, MD 21010–5423

(Received 30 May, 1998; Revised 23 June, 1998)

The normal mode frequencies and the corresponding vibrational assignments of the *s-trans* and *gauche* conformers of isopropylphosphine-d0 and isopropylphosphine-P,P-d2 are examined theoretically using the Gaussian 94 set of quantum chemistry codes at the MP2/6–311G** and DFT/B3LYP/6–311G** levels of theory. By comparison to experimental normal mode frequencies deduced by Durig and Cox [J. R. Durig and A. W. Cox, Jr., *J. Chem. Phys.* **80,** 2493 (1976)] correction factors for predominant vibrational motions are reported and compared. Energetic differences as well as thermodynamic function differences between the *s-trans-* and *gauche*-conformers are considered. It is found at the MP2 and DFT levels of theory that the *gauche* conformer is more stable by 0.54 kJ/mol and 0.28 kJ/mol, respectively.

Keywords: Vibrations; Normal mode frequencies; Infrared spectra; Isopropylphosphine; Isotopomers

1. INTRODUCTION

We have recently considered, from a theoretical point of view, the infrared spectra of two primary amines, methylamine[1] and ethylamine[2], along with their corresponding ammonium ions as well as the primary amine isopropylamine[3]. In order to resolve ambiguities in making assignments of vibrational modes we examined several isotopomers of these compounds.

---

* NAS/NRC Fellow (1997–98)

† Author to whom correspondence should be sent. [Permanent address: Department of Chemistry / Lehigh University / Bethlehem, PA 18015–3172; email: dz00@lehigh.edu.]

In the present study we continue this work with the primary phosphine isopropylphosphine [1-methylethylphosphine].

It has been our experience that making unambiguous normal mode assignments requires some care. One method for resolving ambiguities is to examine a series of isotopomers of the compound of interest. The requirement that the normal mode assignments be consistent with all possible isotopic shifts in the infrared spectrum (both calculated and experimental) imposes severe restrictions on defining the localized motions in the vibrational modes.

In this report we continue our earlier efforts with the consideration of two isotopomers of isopropylphosphine, isopropylphosphine-d0 and isopropylphosphine-P,P-d2, in the *trans* (lone pair of electrons on P *trans* to α-CH bond) and *gauche* (lone pair of electrons on P *gauche* to α-CH bond) conformations. Our approach is to use the Gaussian 94 electronic structure software package[4] at the MP2/6–311G**[5,6] and DFT/B3LYP/6–311G** levels of theory[7,8]. Optimized geometries were deduced for the *s-trans* and *gauche* conformers and this step was followed with the determination of the 33 normal mode vibrational frequencies for each isotopomer. Durig and Cox[9] have published experimental infrared spectra and normal mode assignments for $(CH_3)_2CHPH_2$ and $(CH_3)_2CHPD_2$. Using the available experimental frequencies[9] for the *s-trans* and *gauche* conformers of $(CH_3)_2CHPH_2$ and $(CH_3)_2CHPD_2$, we determined correction factors for each unique vibrational motion.

2. COMPUTATIONAL DETAILS

The Gaussian 94 electronic structure methodology[4] was used to determine the optimized geometries of *gauche*- and *s-trans*-isopropylphosphine at the MP2/6–311G**[5] and DFT/B3LYP/6–311G**[6,7] levels of theory. The DFT calculations used the B3LYP functional formed by combining Becke's three-parameter exchange functional[6] and the nonlocal correlation functional of Lee, Yang and Parr[7]. The optimized geometries that were found are displayed in Figure 1. The optimized geometries are reported in Table I along with a comparison with the microwave experimental values for some geometrical structural parameters of the *gauche* conformer that were obtained by Durig and Li[10]. It should be emphasized that the optimized geometrical coordinates which are reported correspond to positions at which there is a minimum in the potential energy surface. In the microwave experiment rotational motion which occurs in ~10^{-10}s will be averaged over the vibrational motion which occurs in ~10^{-13}s. As a result the experimental values of the geometrical coordinates correspond to vibrational averages over the actual potential function. These two different types of coordinates would indeed be identical if the potential function would be exactly harmonic and would show deviations as the potential function for a given coordinate motion would become anharmonic.

Although here the agreement between the theoretical and experimental coordinates is very reasonable, part of the discrepancy is attributed to the theoretical and experimental geometrical coordinates being defined in slightly different ways. Both the MP2 and DFT/B3LYP levels of calculation produce values in very good agreement with the values that were deduced from the microwave experiment in which only the *gauche* conformer was observed. The microwave experiment was performed on the -d0 and -d2 isotopomers with each sample maintained at dry ice temperature (-78.5°C). At 194.65 K the MP2/6–311G** value of ΔG°for the g → tr equilibrium is found to be +0.47 kJ $mol^{-1}$from which we obtain the *trans*: *gauche* ratio N_{tr}/N_g= (1/2) exp(-301.8 J mol^{-1}/RT) = 0.37 [the corresponding value of N_{tr}/N_g = 0.39 at 25°C]. The dipole moments of the two conformers are quite similar – e.g. at the MP2 level of calculation μ_{gauche} = 1.3447 D and μ_{trans} = 1.3695 D. From analysis of the microwave spectra of isopropylphosphine-d0 and isopropylphosphine-d2 Durig and Li[10] deduced the dipole moment of the *gauche* conformer to be 1.23 D. The calculated values of the A, B and C rotational constants for the *gauche* conformers of the -d0 and -d2 isotopomers, as determined at the MP2/6311G** and DFT/B3LYP/6–311G** levels of theory, are reported in Table II and compared to the experimentally determined values of Durig and Li[10]. The agreement with experiment is very good for both methods, but the MP2 level of calculation is in slightly better agreement with experiment. Comparison with experiment for the *s-trans* conformer was not possible since no experimental structural data could be found in the literature. In contrast for isopropylamine[3] the *s-trans* conformer, not the *gauche* conformer as was observed here for isopropylphosphine, was found to be the more stable conformer.

TABLE I Calculated and experimental average ground state geometries and total energies for *s-trans-* and *s-gauche-*isopropylphospine-d0

Geometrical Coordinate	*s-trans-*$(CH_3)_2CH\text{-}PH_2$			*gauche-*$(CH_3)_2CH\text{-}PH_2$		
	*MP2/ 6–311G***	*DFT/B3LYP/ 6–311G***	*Expt.*	*MP2/ 6–311G***	*DFT/B3LYP/ 6–311G***	*Expt.*[a]
r(C-C)/pm	154.5	153.4	-----	153.1	153.4	152.7
r(C-P)/pm	186.8	189.2	-----	186.6	188.8	187.8
r(C-H)/pm	109.5	109.4	-----	109.5	109.6	109.
r(P-H)/pm	141.3	142.5	-----	141.4	142.6	141.4
∠C-C-P/°	109.4	109.6	-----	109. 1	109.3	109.5
∠C-C-C°	111.1	111.6	-----	111.0	111.7	111.8
∠C-P-H/°	97.2	97.4	-----	96.6	97.3	97.5
∠H-P-H/°	94.4	93.5	-----	94. 1	93.4	93.4
dihedral∠ of lone pair on P	0	0	-----	+57.3, –57.3	+58.4, –58.4	-----
τ (∠ between C-P axis and PH_2 plane)	79.3	79.2	-----	80.3	79.3	-----
Total energy/a.u.[b]	-460.093870	-461.040099	-----	-460.094075	-461.040204	-----

[a] J. R. Durig and Y. S. Li, *J. Mol. Spectrosc.* **70**, 27 (1978).

[b] Electronic energy plus zero-point vibrational energy (vibrational frequencies are scaled using factors reported in Tables V or VI)

TABLE II Calculated and experimental rotational constants for *gauche*-$(CH_3)_2CH$-PH_2 and *gauche*-$(CH_3)_2CH$-PD_2

Rotational Constant/GHz	*gauche*-$(CH_3)_2CH$-PH_2			*gauche*-$(CH_3)_2CH$-PD_2		
	*MP2/6–311G***	*DFT/B3LYP/6–311G***	*Expt.*[a]	*MP2/6–311G***	*DFT/B3LYP/6–311G***	*Expt.*[a]
A	7.66939	7.59991	7.63334 ± 0.00009	7.26386	7.19445	7.2264 ± 0.00005
B	4.24389	4.15608	4.24336 ± 0.00002	4.04050	3.95290	4.04106 ± 0.00002
C	3.05371	2.99326	3.04584 ± 0.00002	2.95383	2.89322	2.94685 ± 0.00002

[a] J. R. Durig and Y. S. Li, *J. Mol. Spectrosc.* **70**, 27 (1978).

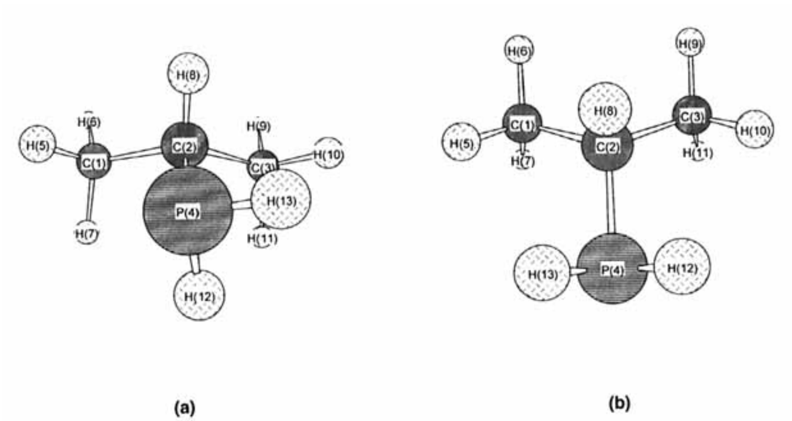


FIGURE 1 Optimized geometries for: (a) gauche- isopropylphosphine and (b) s-trans- isopropylphosphine

3. ENERGETICS AND THERMODYNAMIC FUNCTIONS FOR THE *gauche* → *s-trans* EQUILIBRIUM

The *gauche* and *s-trans* conformers for isopropylphosphine were optimized at the MP2 and DFT/B3LYP levels of theory using a 6–311G** basis set. The energetics based on electronic energy and zero-point vibrational energy contributions (with the vibrational frequencies using the set of scaling factors reported in Table V or VI) indicate that the *gauche* conformer is more stable than the s-trans conformer by 0.54 kJ mol^{-1}[E_{tr}- E_g = (– 460.093870 a.u.)-(-460.094075 a.u.) = 2.05 × 10^{-4} a.u.] at the MP2 level of theory and 0.28 kJ mol^{-1} [E_{tr}- E_g = (-461.040099 a.u.)-(-461.040204 a.u.) = 1.05 × 10^{-4} a.u.] at the DFT level of theory. In order to examine the effect of the inclusion of additional electron correlation, an MP4-level calculation was performed at the MP2-optimized geometry for the *gauche* and *s-trans* conformers; using the MP4-electronic energy with the MP2-determined zero-point energy for each conformer, led to the *gauche* form being more stable by 0.47 kJ mol^{-1}.

Standard state changes in thermodynamic functions for the *gauche* → *s-trans* equilibrium can readily be determined by taking into account the translational, vibrational and rotational contributions. Since the microwave experimental study of Durig and Li was carried out at dry ice temperature (-78.5°C) we determined several changes in thermodynamic functions at 194.15 K. At this temperature the enthalpy change, ΔH°, is 0.64 kJ mol^{-1} [(-460.090213 a.u.) – (-460.090458 a.u.)=2.45 × 10^{-4} a.u.] at the MP2 level of theory and 0.34 kJ mol^{-1}[(-461.036449 a.u.) – (-461.036578 a.u.)= 1.29 × 10^{-4} a.u.] at the DFT level of theory. The change in entropy, ΔS°, is 0.90 J K^{-1} mol^{-1} [279.45 J $K^{-1}mol^{-1}$ – 278.55 J K^{-1} mol^{-1}] at the MP2 level of theory and 0.40 J K^{-1} mol^{-1} [279.41 J $K^{-1}mol^{-1}$ – 279.01 J K^{-1} mol^{-1}] at the DFT level. The change in Gibbs free energy, ΔG°, is 0.47 kJ mol^{-1} [(-460.110930 a.u.) – (-460.111109 a.u.)= 1.79 × 10^{-4} a.u.] at the MP2 level of theory and 0.26 kJ mol^{-1} [(-461.057164 a.u.) – (-461.057264 a.u.)= 1.00 × 10^{-4} a.u] at the DFT level of theory. This observation that the *gauche* confomer is more stable than the *trans* conformer is consistent with the microwave experimental results of Durig and Li[10] who were successful in detecting the *gauche* confomer but not the *trans* conformer. Once ΔG° is known, the ratio *tr*:*g* can be determined from $N_{tr}/N_g = \exp(-\Delta G°/RT)$ which at –78.5 °C yields a numerical value of 0.75 using the MP2 calculated value of ΔG°. However, since this ratio would apply to the two equivalent *gauche* conformers, g and g′, the actual *trans: gauche* ratio is $N_{trans}/N_{gauche} = 0.37$.

4. INFRARED SPECTRA AND NORMAL MODES OF *S-TRANS*- AND *GAUCHE*-ISOPROPYLPHOSHINE

In this section we report the normal mode frequencies that were calculated, describe the scaling of the normal modes and report the scaled normal mode frequencies. All results dealing with these points are tabulated in Tables 3–6. We follow an approach of scaling of the calculated frequencies to experimental frequencies developed by Hameka and Jensen[11,12]. This approach works by first deducing a set of individual scaling constants for given vibrational motions by taking the ratio of the experimental value:the theoretical value. This step is then followed by the determination of global scaling factors for the unique vibrational motions of the molecule under study by averaging over all similar vibrational motions, e.g. all C-H stretches in the molecule.

TABLE III Computed and experimental frequencies (cm^{-1}) for nondeuterated isopropylphosphine (IR intensities in units of km/mol are listed in parentheses) (a) *s-trans* – $(CH_3)_2CH\text{-}PH_2$ (b) *gauche* -$(CH_3)_2CH\text{-}PH_2$. Frequencies designated with an (*) differ experimentally for the *trans* and *gauche* conformers.

Sym-metry	*Vib. No*	*a*					*b*					*Assign-ment*
		MP2	*DFT/ B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*MP2*	*DFT/B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	
A′	ν_1	3156(30)	3088(43)	2973(vs)	2970	2965	3161(26)	3095(32)	2973(vs)	2975	2972	CH_3 a-str
	ν_2	3150(46)	3079(56)	2960(vs)	2964	2956	3148(41)	3076(57)	2960(vs)	2962	2954	CH_3 a-str
	ν_3	3101(5)	3040(3)	2932(s)	2943	2942	3078(9)	3019(35)	2932(s)	2921	2922	α-C-H str
	ν_4	3062(20)	3018(28)	2875(s)	2881	2898	3063(23)	3013(8)	2875(s)	2882	2893	CH_3 s-str
	ν_5	2484(71)	2364(76)	2288(vvs)*	2292	2293	2477(62)	2356(68)	2297(vvs)*	2286	2285	P-H s-str
	ν_6	1525(14)	1510(12)	1471(m)	1474	1474	1523(13)	1507(5)	1471(m)	1472	1471	CH_3 bend
	ν_7	1520(5)	1504(12)	1451(m)	1469	1468	1521(6)	1505(15)	1451(m)	1470	1469	CH_3 bend
	ν_8	1437(3)	1423(3)	1389(m)	1389	1389	1436(4)	1424(4)	1389(m)	1388	1390	CH_3 bend
	ν_9	1302(25)	1270(28)	1256(m)	1216	1204	1308(5)	1285(8)	1256(m)	1222	1219	α-C-H bend
	ν_{10}	1207(5)	1183(9)	1114(m)	1181	1177	1207(0)	1184(1)	1114(m)	1181	1178	CH_3 rock
	ν_{11}	1141(21)	1113(16)	1077(s)	1081	1080	1133(21)	1106(17)	1077(s)	1073	1074	PH_2 scissor
	ν_{12}	1092(16)	1072(13)	1066(s)	1069	1067	1108(18)	1089(18)	1066(s)	1084	1084	CH_3 rock
	ν_{13}	933(3)	897(4)	892(w)	916	912	931(1)	893(2)	892(w)	914	908	C-C str (in-phase)
	ν_{14}	820(25)	797(22)	813(s)	802	801	842(27)	821(18)	813(s)	824	825	PH_2 wag

Sym-metry	*Vib. No*	*a*					*b*					*Assign-ment*
		MP2	*DFT/ B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*MP2*	*DFT/B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	
	ν_{15}	650(3)	610(2)	606(w)	623	619	633(3)	593(2)	606(w)	606	601	C-P str
	ν_{16}	395(1)	392(1)	388(w)	388	387	397(0)	396(0)	388(w)	390	391	C-C-C bend
	ν_{17}	321(0)	314(0)	325(m)	340	342	333(0)	324(1)	325(m)	353	353	C-C-P bend
	ν_{18}	264(0)	245(0)	287(w)	283	278	274(0)	254(0)	287(w)	294	288	CH_3 torsion (in-phase)
A″	ν_{19}	3154(17)	3084(23)	2969(vs)	2968	2961	3160(15)	3091(22)	2969(vs)	2974	2968	CH_3 a-str
	ν_{20}	3147(0)	3073(1)	2954(vs)	2961	2951	3142(14)	3068(10)	2954(vs)	2957	2946	CH_3 a-str
	ν_{21}	3060(27)	3014(29)	2895(s)	2879	2894	3058(27)	3010(33)	2895(s)	2878	2890	CH_3 s-str
	ν_{22}	2491(83)	2370(89)	2288(vvs)*	2298	2299	2488(82)	2367(87)	2299(vvs)*	2296	2296	P-H a-str
	ν_{23}	1509(3)	1493(4)	1471(m)	1459	1457	1510(5)	1494(5)	1471(m)	1460	1458	CH_3 bend
	ν_{24}	1504(0)	1491(0)	1465(m)	1454	1456	1501(0)	1488(0)	1465(m)	1451	1453	CH_3 bend
	ν_{25}	1417(5)	1404(6)	1372(m)	1370	1371	1417(5)	1404(6)	1372(m)	1370	1371	CH_3 bend
	ν_{26}	1359(0)	1347(0)	1234(w)	1270	1277	1348(0)	1338(0)	1234(w)	1259	1269	α-C-H bend
	ν_{27}	1161(3)	1127(1)	1164(vw)	1140	1146	1164(7)	1133(7)	1164(vw)	1143	1152	C-C str (out-of-phase)
	ν_{28}	998(0)	975(0)	1050(m)	977	970	993(1)	971(0)	1050(m)	972	966	CH_3 rock
	ν_{29}	945(2)	937(2)	924(vw)	925	933	945(3)	938(3)	924(vw)	925	933	CH_3 rock
	ν_{30}	849(9)	826(7)	809(s)	813	814	840(13)	815(17)	809(s)	805	804	PH_2 twist

Sym-metry	*Vib. No*	*a*					*b*					*Assign-ment*
		MP2	*DFT/ B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*MP2*	*DFT/B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	
	ν_{31}	274(1)	267(1)	322(m)	290	291	298(1)	288(1)	322(m)	316	313	C-C-P bend
	ν_{32}	242(0)	233(0)	266(vw)	260	264	241(0)	230(0)	266(vw)	259	261	CH_3 torsion (out-of-phase)
	ν_{33}	166(3)	165(3)	163(s)	162	166	169(3)	159(3)	163(s)	164	160	PH_2 torsion
				σ	23	24				22	23	

TABLE IV Computed and experimental frequencies (cm^{-1}) for isopropylphosphine-P,P-d2 (IR intensities in units of km/mol are listed in parentheses) (a) *s-trans* -$(CH_3)_2CH$-PD_2 (b) *gauche* -$(CH_3)_2CH$-PD_2. Frequencies designated with an (*) differ experimentally between the *trans* and *gauche* conformers.

		a					*b*					
Symmetry	*Vib. No*	*MP2*	*DFT/ B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*MP2*	*DFT/B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*Assignment*
A′	ν_1	3156(29)	3088(42)	2973(vs)	2970	2965	3161(25)	3095(32)	2973(vs)	2975	2972	CH_3 a-str
	ν_2	3150(46)	3079(56)	2960(vs)	2964	2956	3148(41)	3076(57)	2960(vs)	2962	2954	CH_3 a-str
	ν_3	3101(5)	3040(3)	2932(s)	2943	2942	3078(8)	3019(35)	2932(s)	2921	2922	α-C-H str
	ν_4	3062(21)	3018(29)	2876(s)	2881	2898	3063(23)	3013(7)	2876(s)	2882	2893	CH_3 s-str
	ν_5	1781(71)	1695(40)	1663(vvs)*	1663	1664	1777(33)	1690(36)	1668(vvs)*	1660	1659	P-D s-str
	ν_6	1525(14)	1510(12)	1468(m)	1474	1474	1523(14)	1507(5)	1468(m)	1472	1471	CH_3 bend
	ν_7	1520(6)	1504(9)	1448(m)	1469	1468	1521(6)	1505(16)	1448(m)	1470	1469	CH_3 bend
	ν_8	1437(3)	1423(3)	1389(m)	1389	1389	1436(4)	1423(4)	1389(m)	1388	1389	CH_3 bend
	ν_9	1301(24)	1269(27)	1247(m)	1215	1203	1305(6)	1282(8)	1247(m)	1219	1216	α-C-H bend
	ν_{10}	1206(3)	1181(7)	1103(w)	1180	1175	1206(1)	1183(2)	1103(w)	1180	1177	CH_3 rock
	ν_{11}	818(13)	798(10)	784(m)	784	789	817(12)	789(9)	784(m)	784	780	PD_2 scissor
	ν_{12}	1081(8)	1061(6)	1046(s)	1058	1056	1084(11)	1069(12)	1046(s)	1061	1064	CH_3 rock
	ν_{13}	927(2)	889(1)	888(w)	910	904	929(2)	890(2)	888(w)	912	905	C-C str (in-phase)
	ν_{14}	685(20)	656(19)	661(s)	661	636	638(18)	660(7)	615(s)	615	640	PD_2 wag
	ν_{15}	591(3)	565(2)	578(w)	566	573	599(4)	568(2)	578(w)	574	576	C-P str

		a					*b*					
Sym-metry	*Vib. No*	*MP2*	*DFT/ B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*MP2*	*DFT/B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*Assign-ment*
	ν_{16}	387(0)	384(0)	380(w)	380	379	384(0)	383(0)	380(w)	377	378	C-C-C bend
	ν_{17}	319(0)	313(0)	314(m)	338	341	324(1)	315(1)	314(m)	343	343	C-C-P bend
	ν_{18}	263(0)	244(0)	278(w)	282	277	272(0)	253(0)	278(w)	292	287	CH_3 torsion (in-phase)
A″	ν_{19}	3154(17)	3084(23)	2969(vs)	2968	2961	3160(15)	3091(21)	2969(vs)	2974	2968	CH_3 a-str
	ν_{20}	3147(0)	3073(1)	2953(vs)	2961	2951	3142(14)	3068(10)	2953(vs)	2957	2946	CH_3 a-str
	ν_{21}	3060(26)	3014(29)	2892(s)	2879	2894	3058(27)	3010(33)	2892(s)	2878	2890	CH_3 s-str
	ν_{22}	1792(42)	1705(45)	1663(vvs)*	1674	1674	1789(42)	1702(44)	1673.5(vvs)*	1671	1671	P-D a-str
	ν_{23}	1509(3)	1493(4)	1468(m)	1459	1457	1510(5)	1494(6)	1468(m)	1460	1458	CH_3 bend
	ν_{24}	1504(0)	1491(0)	1462(m)	1454	1456	1501(0)	1488(0)	1462(m)	1451	1453	CH_3 bend
	ν_{25}	1417(6)	1404(7)	1372(m)	1370	1371	1416(5)	1404(6)	1372(m)	1369	1371	CH_3 bend
	ν_{26}	1358(0)	1346(0)	1225(w)	1269	1276	1347(0)	1337(0)	1225(w)	1258	1268	α-C-H bend
	ν_{27}	1148(1)	1114(0)	1163(vw)	1127	1133	1152(2)	1119(2)	1163(vw)	1131	1138	C-C str (out-of-phase)
	ν_{28}	996(0)	975(0)	1038(s)	975	970	992(0)	971(0)	1038(s)	971	966	CH_3 rock
	ν_{29}	944(2)	936(2)	924(vw)	924	932	943(2)	936(2)	924(vw)	923	932	CH_3 rock
	ν_{30}	636(5)	618(4)	615(s)	613	638	687(6)	618(15)	661(s)	663	638	PD_2 twist
	ν_{31}	264(1)	258(1)	314(m)	280	281	287(1)	279(1)	314(m)	304	304	C-C-P bend

		a					b					
Symmetry	*Vib. No*	*MP2*	*DFT/ B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*MP2*	*DFT/B3LYP*	*exptal*	*corrected MP2*	*corrected DFT/B3LYP*	*Assignment*
	ν_{32}	234(0)	228(0)	256(vw)	251	259	238(0)	229(0)	256(vw)	255	260	CH_3 torsion (out-of-phase)
	ν_{33}	126(0)	124(2)	125(s)	12 5	128	127(2)	119(2)	125(s)	126	12 2	PD_2 torsion
				σ	23	25				22	23	

TABLE V Correction factors for MP2/6–311G** level of calculation based on consideration of the *s-trans* and *gauche* conformers of isopropylphosphine-d0 and isopropylphosphine-P,P-d2

Vibrational mode	*Correction factor*
CH_3 str	0.9410
α-C-H str	0.9490
P-H str	0.9227
P-D str	0.9340
CH_3 bend	0.9667
α-C-H bend	0.9342
CH_3 rock	0.9786
PH_2 scissor	0.9472
PD_2 scissor	0.9590
C-C str	0.9816
PH_2 wag	0.9785
PD_2 wag	0.9645
PH_2 twist	0.9580
PD_2 twist	0.9646
C-P str	0.9581
C-C-P bend	1.0601
C-C-C bend	0.9828
CH_3 torsion	1.0733
PH_2 torsion	0.9732
PD_2 torsion	0.9882

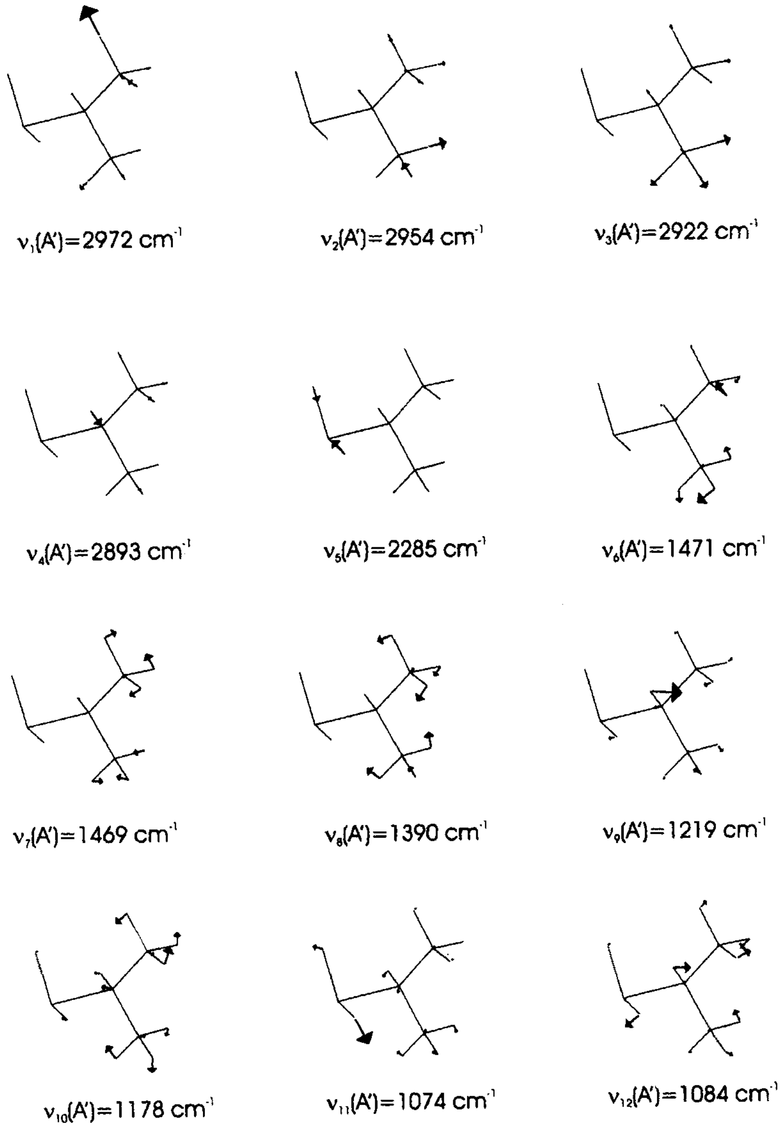
TABLE VI Correction factors for DFT/6–311G** level of calculation based on consideration of the *s-trans* and *gauche* conformers of isopropylphosphine-d0 and isopropyphosphine-P,P-d2

Vibrational mode	*Correction factor*
CH_3 str	0.9602
α-C-H str	0.9678
P-H str	0.9699
P-D str	0.9817
CH_3 bend	0.9762
α-C-H bend	0.9483
CH_3 rock	0.9952
PH_2 scissor	0.9707
PD_2 scissor	0.9881
C-C str	1.0167

Vibrational mode	*Correction factor*
PH_2 wag	1.0052
PD_2 wag	0.9697
PH_2 twist	0.9860
PD_2 twist	1.0324
C-P str	1.0140
C-C-P bend	1.0881
C-C-C bend	0.9878
CH_3 torsion	1.1348
PH_2 torsion	1.0065
PD_2 torsion	1.0292

In Table III the predicted normal mode frequencies and corresponding infrared intensities that were determined at the MP2/6–311G** and DFT/B3LYP/6–311G** levels of theory are reported along with the experimentally assigned frequencies of Durig and Cox[7] for the *gauche* and *s-trans* conformers of $(CH_3)_2CH\text{-}PH_2$. In Table IV similar values are reported for the *gauche* and *s-trans* conformers of the deuterated isotopomer $(CH_3)_2CHPD_2$. Based on the determination of individual scaling constants from the frequencies reported in Tables 3 and 4, global scaling constants for 15 unique vibrational modes were determined and those values are reported in Tables 5 and 6 for the isotopomers that were considered. It is worth noting that the scaling factor for the DFT/B3LYP/6–311G** is slightly larger than for the MP2/6–311G** level of calculation indicating that there is less of a need for scaling than for the MP2/6–311G**. In Tables 3 and 4 the quality of fitting is indicated by the root-mean-square standard deviation, $\sigma = \{\Sigma_i(\nu_{pred,i} - \nu_{calc,i})^2 / N\}^{1/2}$ where N is the number of normal modes (33 for isopropylphosphine), which ranges between 22–25 cm^{-1}, with both levels of calculation giving comparable σ values. The range of σ found is comparable to the range of σ values found for methylamine[1], ethylamine[2] and isopropylamine[3]. The requirement that the normal mode assignments be consistent with all possible isotopic shifts in the infrared spectrum (both calculated and experimental) imposes severe restrictions on defining the localized motion involved in a particular vibrational mode.

As an aid in the assignments of the normal modes of vibration both the GaussView[13] molecular modeling software and the Svib Vibrational



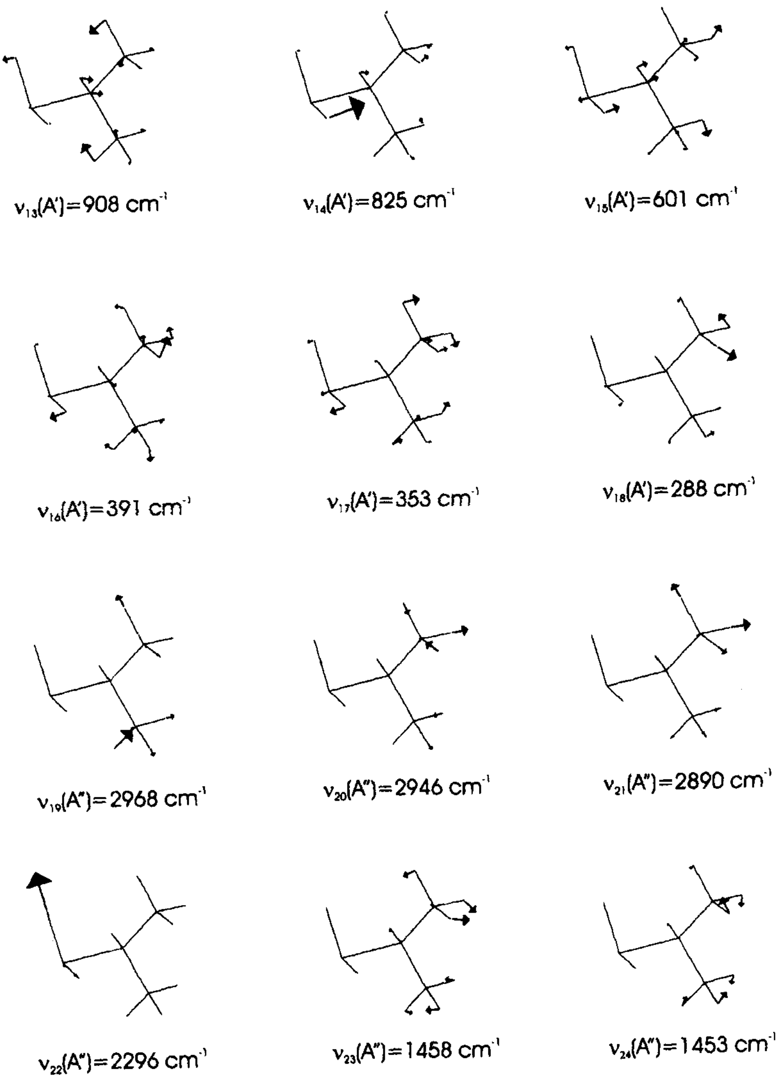
$\nu_1(A')=2972\ \mathrm{cm}^{-1}$ $\nu_2(A')=2954\ \mathrm{cm}^{-1}$ $\nu_3(A')=2922\ \mathrm{cm}^{-1}$

$\nu_4(A')=2893\ \mathrm{cm}^{-1}$ $\nu_5(A')=2285\ \mathrm{cm}^{-1}$ $\nu_6(A')=1471\ \mathrm{cm}^{-1}$

$\nu_7(A')=1469\ \mathrm{cm}^{-1}$ $\nu_8(A')=1390\ \mathrm{cm}^{-1}$ $\nu_9(A')=1219\ \mathrm{cm}^{-1}$

$\nu_{10}(A')=1178\ \mathrm{cm}^{-1}$ $\nu_{11}(A')=1074\ \mathrm{cm}^{-1}$ $\nu_{12}(A')=1084\ \mathrm{cm}^{-1}$

FIGURE 2 Displacement vectors corresponding to the 33 normal modes of vibration of *gauche*-isopropylphosphine. The frequencies are the scaled DFT/B3LYP values that are reported in Table III



$\nu_{13}(A')=908\ \mathrm{cm}^{-1}$ $\nu_{14}(A')=825\ \mathrm{cm}^{-1}$ $\nu_{15}(A')=601\ \mathrm{cm}^{-1}$

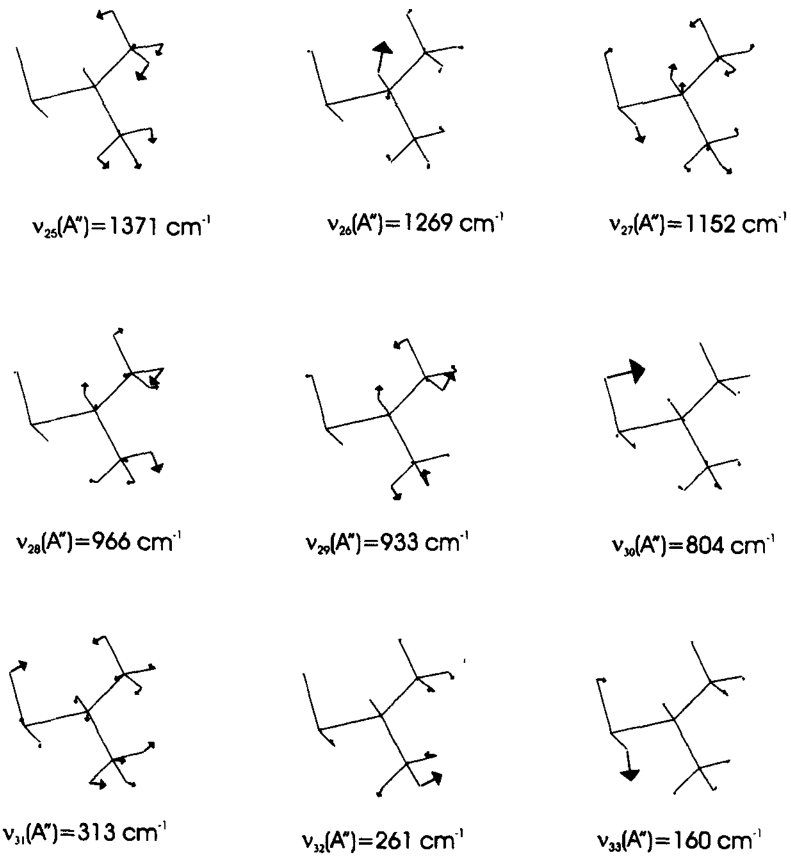
$\nu_{16}(A')=391\ \mathrm{cm}^{-1}$ $\nu_{17}(A')=353\ \mathrm{cm}^{-1}$ $\nu_{18}(A')=288\ \mathrm{cm}^{-1}$

$\nu_{19}(A'')=2968\ \mathrm{cm}^{-1}$ $\nu_{20}(A'')=2946\ \mathrm{cm}^{-1}$ $\nu_{21}(A'')=2890\ \mathrm{cm}^{-1}$

$\nu_{22}(A'')=2296\ \mathrm{cm}^{-1}$ $\nu_{23}(A'')=1458\ \mathrm{cm}^{-1}$ $\nu_{24}(A'')=1453\ \mathrm{cm}^{-1}$

FIGURE 2 Continued

Analysis Program[14] were used for visualizing the normal modes of the molecules which aided us greatly in making the normal mode assignments. The normal mode displacement coordinates for *gauche*-isopropylphos-



$\nu_{25}(A'')=1371\ cm^{-1}$ $\nu_{26}(A'')=1269\ cm^{-1}$ $\nu_{27}(A'')=1152\ cm^{-1}$

$\nu_{28}(A'')=966\ cm^{-1}$ $\nu_{29}(A'')=933\ cm^{-1}$ $\nu_{30}(A'')=804\ cm^{-1}$

$\nu_{31}(A'')=313\ cm^{-1}$ $\nu_{32}(A'')=261\ cm^{-1}$ $\nu_{33}(A'')=160\ cm^{-1}$

FIGURE 2 Continued

phine-d0 are shown in Figure 2. The point group symmetry for *s-trans*-isopropylphosphine is C_S. All vibrations are nondegenerate and of symmetry A′ or A″. The normal mode assignments for the *s-trans* conformers of the -d0 and -d2 isotopomers are given in Table III and IV. For *gauche*-isopropyphosphine there is no symmetry. As a result, all nondegenerate vibrations belong to the same irreducible representation, and vibrations cannot be distinguished by symmetry. However, in displaying the vibrational motions it is possible to make a one-to-one correspondence of the vibrational modes in the *gauche* form to the vibrational modes in the *s-trans* form of isopropylphosphine. In Tables 3 and 4, for the *gauche* -d0 and -d2 isotopomers, vibrations are grouped into the same symmetry format as used for the *trans* conformers where a given vibration is of symmetry A′ or A″. Consistent with past usage we felt it was useful to keep the labels A′ and A″ even though they no longer are symmetry labels in the case of the *gauche* conformers.

With regard to the two conformers of isopropylamine, the vibrational modes that have significant absorption intensities are the P-H and C-H stretching modes, the α-CH bend, the PH_2 scissor, and the PH_2 wag. The phosphino and methyl torsional motions have weak intensities.

This study has considered the prediction of the normal mode vibrational frequencies, normal mode assignments, the predicted infrared spectra, and some energetics of two isotopomers of *s-trans* and *gauche* conformers of isopropylphosphine based on calculations done at the MP2/6–311G** and DFT/B3LYP/6–311G** levels of theory. Based on use of experimentally determined normal mode frequencies, correction constants have been developed for the nondeuterated species and deuteration of the PH_2-group. It is observed that most global correction factors at the MP2 level of theory are approximately 0.95 and at the DFT/B3LYP are approximately 0.97. The *gauche* confomer is found to be more stable than the *s-trans* conformer with the $\Delta H°$ value for the transformation *gauche* → *s-trans* determined to be 0.64 kJ mol^{-1} at the MP2/6311G** level and 0.34 kJ mol-1 at the DFT/B3LYP/6–311G** level which is consistent with the microwave spectral data where only the *gauche* conformer was experimentally detected.

Acknowledgements

We express our appreciation to the U. S. Army Edgewood Research, Development and Engineering Center (ERDEC) for their support of this work as part of the Standoff Detection Project, Project Number 1C162622A553C, Reconnaissance, Detection and Identification. This work was performed during the academic year 1997–98 when DZ held a National Research Council-ERDEC Senior Research Associateship. We are appreciative of the comments of an anonymous referee with regard to a few points, which we have taken into account in our revision of the original version of the manuscript.

References

[1] D. Zeroka and J. O. Jensen, *J. Mol. Struct. (Theochem)*, **425,** 181 (1998).

[2] D. Zeroka, J. O. Jensen and A. C. Samuels, *J. Mol. Struct. (Theochem)*, to be published.

[3] D. Zeroka, J. O. Jensen and A. C. Samuels, *Int. J. of Quantum Chem.*, submitted.

[4] Gaussian 94, Revision E.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres,E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

[5] C. Møller and M. S. Plesset, *Physical Review,* **46,** 618 (1934).

[6] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory* (John Wiley, New York, 1986).

[7] A. D. Becke, *J. Chem. Phys.* **98,** 5648 (1993).

[8] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* **37,** 785 (1988).

[9] J. R. Durig and A. W. Cox, *J. Chem. Phys.* **80,** 2493 (1976).

[10] J. R. Durig and Y. Li, *J. Mol. Spectrosc.* **70,** 27 (1978).

[11] H. F. Hameka, *J. Mol. Struct.(Theochem)* **284,** 189 (1993).

[12] H. F. Hameka and J. O. Jensen, *J. Mol. Struct. (Theochem)* **362,** 329 (1996).

[13] GaussView 1.0 (Gaussian, Inc., 1997).

[14] A. Mukherjee and T. G. Spiro, "The Svib Program: An Expert System for Vibrational Analysis", QCPE Program 656, Indiana University (1995).