

An *ab initio* study of the vibrational frequencies and infrared intensities of CH₂F₂

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The infrared vibrational frequencies and intensities were calculated for methylene fluoride using *ab initio* molecular orbital theory. Calculations were carried out using several split valance basis sets (3-21G, 4-31G, 6-31G, 6-311G) augmented with diffuse functions and several sets of polarization functions. The CID/6-31G(*d*) optimized geometry was found to agree well with the experimental R_e structure and was used for all of the frequency calculations. The atomic polar tensors were calculated by differentiation of the dipole moment at the Hartree–Fock and MP2 levels. The HF/6-311 + + G(3*d,p*) dipole moment is 2.20 D; the dipole moment is 2.12 D at the MP2/6-311 + G(*d,p*) level and is estimated to be 1.90 D at the MP2/6-311 + + G(3*d,3p*) level, compared to the experimental value of $1.9785 \pm .0021$ D. The average error in the calculated harmonic frequencies is 5% at HF/6-311 + + G(3*d,p*), 1.9% at MP2/6-311 + G(*d,p*), and 1.3% at the estimated MP2/6-311 + + G(3*d,3p*) level (compared to the experimental harmonic frequencies). The infrared intensities are more sensitive to the size of the basis set than the frequencies. The average error in the calculated double harmonic IR intensities is 26 km/mol at HF/6-311 + + G(3*d,p*), 7.8 km/mol at MP2/6-311 + G(*d,p*) and 3.1 km/mol at the estimated MP2/6-311 + + G(3*d,3p*) level (compared to the observed values for $A_2, A_4, A_8, A_1 + A_6,$ and $A_3 + A_7 + A_9$).

INTRODUCTION

There has been considerable interest in the vibrational spectrum of methylene fluoride,^{1,2} CH₂F₂, in part due to the high efficiency lasing of methylene fluoride in the FIR region of the spectrum.^{3–5} Gaw, Handy, Palmieri and Esposti⁶ have calculated the harmonic and cubic force field and have found good agreement with available experimental data. The fundamental vibrational frequencies^{2,7–9} and the R_e structure¹⁰ are well established. Infrared intensities have been studied by a number of groups; however, there are significant differences between the various experimental measurements of the IR absorption intensities. Previous theoretical work on IR intensities by semiempirical methods^{11,12} and small basis set *ab initio* calculations,¹¹ have not obtained good agreement with experiment. Recent measurements by Zhang, Gu, Isenor, and Scoles¹ based on Rabi oscillations in molecular beam laser Stark spectroscopy indicate that the transition dipole for ν_9 is considerably higher than found in earlier work.

The accurate calculation of vibrational frequencies requires large basis sets and inclusion of correlation corrections.¹³ The calculation of intensities is even more demanding, requiring an even larger basis set as well as the inclusion of correlation corrections. In previous calculations on CH₃F^{14(a)} good agreement with experiment^{14(b)} was found when very large basis sets were used and electron correlation corrections were included. A similar approach is used in the present work for CH₂F₂.

METHOD

Ab initio molecular orbital calculations were carried out with the GAUSSIAN 86™ series of programs.¹⁵ The vibrational frequencies were determined from second derivatives calculated analytically at the Hartree–Fock level and by numerical central differentiation of analytical gradients for the second order Møller–Plesset (MP2) perturbation theory using a step size of 0.005 Å. Force constants and infrared intensities calculated at the MP2/6-311 + G(*d,p*) level are available in the supplementary material.

The infrared intensities were calculated from the atomic polar tensors (APT, i.e., the dipole moment derivatives). In the double harmonic approximation, the intensities, in kilometers per mole, are given by

$$A_i = \frac{N\pi d_i}{3c^2} \left| \frac{d\mu}{dQ_i} \right|^2, \quad (1)$$

where N is Avagadro's number, d_i is the degeneracy *i*th fundamental, c is the speed of light, and $d\mu/dQ_i$ is the dipole moment derivative with respect to the corresponding normal mode coordinate Q_i . At the Hartree–Fock level the dipole moment derivatives with respect to the coordinates of the nuclei were calculated analytically; at the MP2 level the dipole moment derivatives were determined numerically by central differentiation of the dipole moment with step size of 0.005 Å. The APTs calculated at the MP2/6-311 + G(*d,p*) level are available in the supplementary material. The APTs are then transformed to the normal mode coordinate system (Q_i), to get the dipole moment derivatives with respect to the normal modes.

Calculations at the MP2 level with large basis sets are

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TABLE I. Calculated and experimental geometries (Ångstroms and degrees).

Parameter	HF/6-31G(d)	CID/6-31G(d)	Exp. R_e^a	Exp. R_0^b
$R(\text{CH})$	1.0781	1.087	1.084 ± 0.003	1.093 ± 0.003
$R(\text{CF})$	1.3382	1.353	1.3508 ± 0.0005	1.357 ± 0.001
$\angle \text{HCH}$	112.46	112.60	112.8 ± 0.03	113.67 ± 0.17
$\angle \text{FCF}$	108.60	108.67	108.49 ± 0.06	108.32 ± 0.05

^a See Ref. 10.^b See Ref. 16.

computationally very costly; hence MP2 frequencies and intensities were not calculated for basis sets larger than 6-311 + G(d,p). However, the MP2/6-311 + + G($3d,p$) and the MP2/6-311 + + G($3d,3p$) dipole moments,

frequencies, and intensities were estimated from the HF/6-311 + + G($3d,p$), MP2/6-311 + G(d,p), HF/6-311 + G(d,p), HF/6-31 + G(d,p), and HF/6-31 + G($d,3p$) data, according to the formulas:

$$\text{est MP2/6-311 + G}(d,p) = \text{MP2/6-31G}(d) + \text{HF/6-311 + G}(d,p) - \text{HF/6-31G}(d) \quad (2)$$

$$\begin{aligned} \text{est MP2/6-311 + + G}(3d,p) = & \text{MP2/6-311 + G}(d,p) \\ & + \text{HF/6-311 + + G}(3d,p) - \text{HF/6-311 + G}(d,p), \end{aligned} \quad (3)$$

$$\begin{aligned} \text{est MP2/6-311 + + G}(3d,3p) = & \text{MP2/6-311 + G}(d,p) \\ & + \text{HF/6-311 + + G}(3d,p) - \text{HF/6-311 + G}(d,p) \\ & + \text{HF/6-31 + G}(d,3p) - \text{HF/6-31 + G}(d,p). \end{aligned} \quad (4)$$

TABLE II. Calculated energies and dipole moments.

Calculational level	Energy (hartrees)	Dipole moment (Debye)
HF/STO-3G	-234.624 537	1.27
HF/3-21G	-236.608 148	2.40
HF/4-31G	-237.591 813	2.67
HF/6-31G	-237.821 282	2.66
HF/6-31G(d)	-237.895 798	2.12
HF/6-31G($2d$)	-237.897 454	2.01
HF/6-31G($3d$)	-237.910 887	2.13
HF/6-31 + G	-237.832 968	2.84
HF/6-31 + G(d)	-237.909 836	2.33
HF/6-31 + G(d,p)	-237.913 224	2.34
HF/6-31 + G($d,2p$)	-237.913 585	2.32
HF/6-31 + + G($d,2p$)	-237.913 706	2.31
HF/6-31 + G($d,3p$)	-237.914 432	2.28
HF/6-31 + G($2d,p$)	-237.917 039	2.20
HF/6-31 + G($3d,p$)	-237.921 526	2.19
HF/6-311G	-237.894 830	2.66
HF/6-311G(d)	-237.962 845	2.25
HF/6-311G(d,p)	-237.966 705	2.25
HF/6-311 + G	-237.899 595	2.75
HF/6-311 + G(d)	-237.970 349	2.36
HF/6-311 + G(d,p)	-237.973 505	2.36
HF/6-311 + + G(d,p)	-237.973 622	2.36
HF/6-311 + + G($2d,p$)	-237.979 139	2.24
HF/6-311 + + G($2dd',p$)	-237.980 248	2.22
HF/6-311 + + G($3d,p$)	-237.982 436	2.20
MP2/6-31G(d)	-238.373 072	1.85
MP2/6-311 + G(d,p)	-238.591 055	2.12
est MP2/6-311 + + G($3d,p$)	-238.599 986	1.96
est MP2/6-311 + + G($3d,3p$)	-238.601 194	1.90
CID/6-31G(d)	-238.339 566	
Experimental ^a		$1.96 \pm .02$
Experimental ^b		$1.9785 \pm .0021$

^a See Ref. 17.^b See Ref. 18.

RESULTS AND DISCUSSION

Geometry

The experimental and calculated geometries for methylene fluoride are summarized in Table I. The HF/6-31G(*d*) geometry is within 0.002 Å and 0.5° of the HF/6-311G(*d,p*).⁶ Correlation corrections have little effect on the angles but lengthen the CH bonds by 0.009 Å and the CF bonds by 0.015 Å. The CID/6-31G(*d*) structure is in very good agreement with the experimental equilibrium structure¹⁰ ($\Delta R = 0.003$ Å and $\Delta\Theta = 0.2^\circ$). The experimental R_0 structure has significantly longer bonds ($\Delta R = 0.006$ – 0.009 Å) and a larger HCH angle ($\Delta\Theta = 0.8^\circ$) than the R_e geometry, due to vibrational anharmonicity.

Dipole moment

The energies and dipole moments for the molecular orbital calculations with various basis sets are summarized in Table II. All of the Hartree–Fock level calculations overestimate the dipole moment. As found earlier for CH₃F,^{14(a)} diffuse functions and multiple sets of polarization functions are needed for an accurate calculation of the dipole moment. The calculated dipole moment is the same at the HF/6-31G and HF/6-311G levels. The addition of diffuse functions to

the heavy atoms (carbon and fluorines) increases the dipole moment by 0.09 to 0.18 D, but diffuse functions on the hydrogen atoms do not change the dipole moment appreciably ($|\Delta\mu| \leq 0.01$ D). The addition of one set of *d* polarization functions to the heavy atoms reduces the dipole moment by 0.39 to 0.54 D. The addition of a second and a third set decreases it by up to 0.16 D, with the exception of changing from 6-31G(2*d*) to 6-31G(3*d*) where the dipole moment increases by 0.12 D. The addition of *p* polarization functions to the hydrogen atoms has only a very small effect ($|\Delta\mu| \leq 0.03$ D). The dipole moment for the largest basis set (6-311 + + G(3*d,p*)) is calculated to be 12.3% too high. The inclusion of MP2 correlation corrections decreases the dipole moment by 0.27 D with the 6-31G(*d*) basis set, and by 0.24 D with the 6-311 + G(*d,p*) basis set. The estimated MP2/6-311 + + G(3*d,p*) dipole moment is 1.96 D, while the estimated MP2/6-311 + + G(3*d,3p*) dipole moment is 1.90 D; both are in excellent agreement with experimental value, 1.9785 ± 0.0021 D.¹⁷

Frequencies

The calculated and experimental frequencies are summarized in Table III; selected calculations are compared with experiment in Fig. 1. Blom and Müller⁹ obtained esti-

TABLE III. Calculated and experimental absorption frequencies of CH₂F₂ (cm⁻¹).

Calculational level	$A_1 \nu_1$ CH ₂ sym stretch	$A_1 \nu_2$ CH ₂ scissor	$A_1 \nu_3$ CF ₂ sym stretch	$A_1 \nu_4$ CF ₂ bend	$A_2 \nu_5$ CH ₂ twist	$B_1 \nu_6$ CH ₂ asym stretch	$B_1 \nu_7$ CH ₂ rock	$B_2 \nu_8$ CH ₂ wag	$B_2 \nu_9$ CF ₂ asym stretch
HF/STO-3G	3671	1732	1371	536	1413	3806	1216	1684	1457
HF/3-21G	3157	1746	1238	546	1443	3215	1308	1679	1319
HF/4-31G	3161	1733	1224	540	1438	3230	1297	1657	1287
HF/6-31G	3182	1730	1237	535	1432	3254	1297	1657	1304
HF/6-31G(<i>d</i>)	3216	1716	1191	561	1412	3288	1309	1639	1197
HF/6-31G(2 <i>d</i>)	3171	1680	1158	560	1398	3249	1290	1608	1149
HF/6-31G(3 <i>d</i>)	3201	1684	1172	565	1396	3271	1292	1602	1163
HF/6-31 + G	3190	1712	1215	531	1407	3263	1276	1628	1273
HF/6-31 + G(<i>d</i>)	3223	1702	1184	560	1415	3294	1295	1617	1178
HF/6-31 + G(<i>d,p</i>)	3206	1686	1185	560	1399	3279	1288	1606	1178
HF/6-31 + G(<i>d,2p</i>)	3183	1677	1184	561	1394	3256	1284	1596	1178
HF/6-31 + + G(<i>d,2p</i>)	3183	1677	1185	561	1395	3256	1284	1597	1178
HF/6-31 + G(<i>d,3p</i>)	3188	1673	1185	562	1394	3259	1283	1591	1179
HF/6-31 + G(2 <i>d,p</i>)	3192	1671	1153	556	1390	3266	1281	1590	1130
HF/6-31 + G(3 <i>d,p</i>)	3201	1673	1168	563	1391	3272	1289	1592	1150
HF/6-311G	3151	1719	1210	534	1420	3218	1297	1649	1261
HF/6-311G(<i>d</i>)	3207	1698	1174	569	1416	3277	1302	1631	1161
HF/6-311G(<i>d,p</i>)	3190	1675	1174	567	1401	3261	1289	1613	1165
HF/6-311 + G	3144	1706	1195	532	1415	3211	1278	1623	1240
HF/6-311 + G(<i>d</i>)	3204	1687	1169	567	1410	3276	1294	1611	1151
HF/6-311 + G(<i>d,p</i>)	3191	1670	1170	566	1395	3261	1281	1594	1155
HF/6-311 + + G(<i>d,p</i>)	3191	1669	1170	566	1394	3261	1282	1595	1155
HF/6-311 + + G(2 <i>d,p</i>)	3174	1670	1160	561	1388	3243	1283	1590	1137
HF/6-311 + + G(2 <i>dd',p</i>)	3172	1670	1159	561	1388	3242	1281	1588	1137
HF/6-311 + + G(3 <i>d,p</i>)	3182	1669	1157	561	1385	3252	1285	1585	1132
MP2/6-31G(<i>d</i>)	3182	1615	1183	531	1310	3263	1221	1531	1203
MP2/6-311 + G(<i>d,p</i>)	3166	1565	1149	538	1306	3246	1198	1498	1141
est MP2/6-311 + + G(3 <i>d,p</i>)	3157	1564	1136	533	1297	3236	1202	1489	1119
est MP2/6-311 + + G(3 <i>d,3p</i>)	3139	1550	1136	535	1292	3216	1197	1474	1120
Experimental harmonic ^c	3071	1539	1124	539	1288	3140	1202	1464	1101
Experimental observed ^{a,b}	2948	1508	1113	529	1262	3014	1178	1435	1090

^a For the frequencies of all bands but ν_3 see Ref. 8.

^b For the frequency of ν_3 see Ref. 11.

^c See Ref. 9.

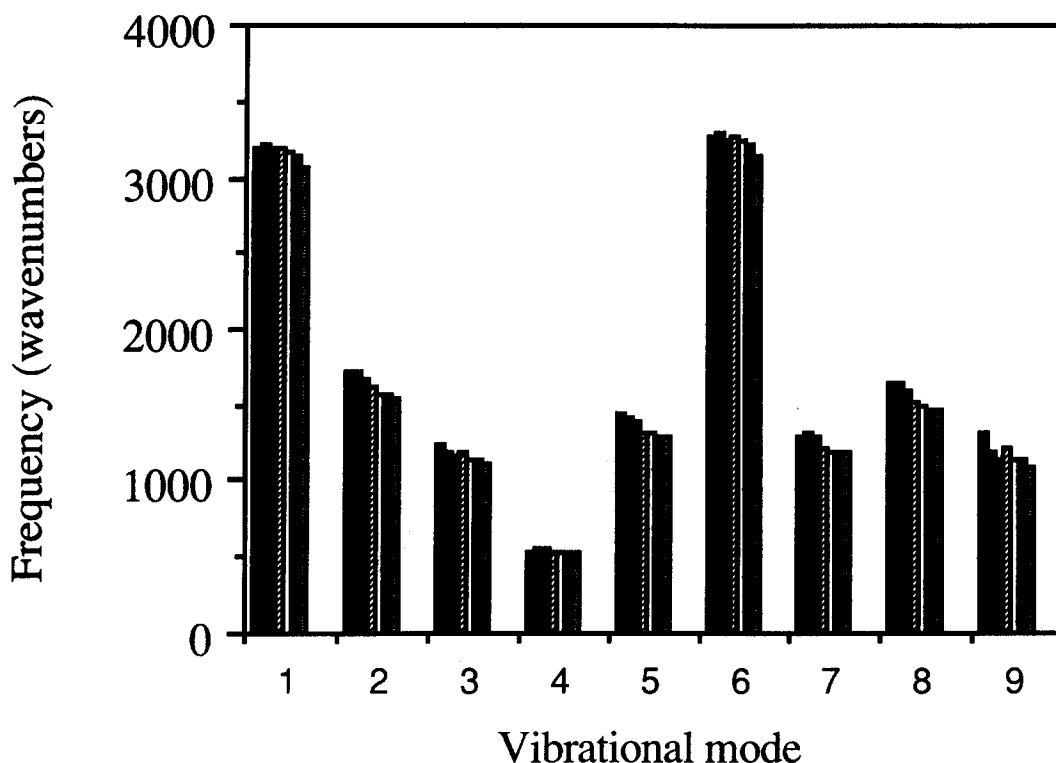


FIG. 1. Calculated and experimental vibrational frequencies for CH_2F_2 . From left to right for each mode: HF/6-31G, HF/6-31G(*d*), HF/6-311 + + G(3*d,p*), MP2/6-31G(*d*), MP2/6-311 + G(*d,p*), estimated MP2/6-311 + + G(3*d,3p*), and experimental harmonic.⁹

mated harmonic frequencies from the experimental anharmonic frequencies using Duncan's¹⁹ empirical parameters for methyl fluoride. The calculated frequencies at all levels are higher than the experimental anharmonic values, and except for the highest levels of calculation, most are higher than the estimated experimental harmonic values. Increasing the size of the basis set from 6-31G to 6-311G decreases the stretching frequencies by 28–39 cm^{-1} and the other modes by up to 12 cm^{-1} . The addition of diffuse functions on heavy atoms to the 6-31G basis set increases the frequencies of the CH_2 stretching modes and decreases the CF_2 stretching modes by 22 to 31 cm^{-1} while lowering the other modes by 4 to 29 cm^{-1} . The addition of diffuse functions to the 6-311G basis set decreases all of the modes by 4 to 26 cm^{-1} . The inclusion of diffuse functions on the hydrogen atoms has little effect on any of the frequencies ($|\Delta\nu| < 1 \text{ cm}^{-1}$). The addition of *d* polarization functions on the heavy atoms has the largest effect on the CF_2 asymmetric stretching mode, lowering it by 89 to 107 cm^{-1} ; it also increases the CH_2 stretching modes by 34 to 65 cm^{-1} . The addition of a second set of *d* functions changes the frequencies by +1 to –48 cm^{-1} with the stretching modes being affected the most; a third set changes the frequencies by –6 to +30 cm^{-1} . In the largest basis set [6-311 + + G(3*d,p*)] the absolute changes for adding a third set of *d* functions are less than ten wave numbers. The addition of one and two sets of *p* polarization functions to the hydrogen atoms changes the frequencies of CH_2 stretching by up to 23 cm^{-1} and a third set changes the frequencies by

less than 5 cm^{-1} . Even though the Hartree–Fock limit is being approached in the largest basis sets, the frequencies are still on average 5% higher than the experimental harmonic values. When correlation corrections are included, the agreement with experiment is improved significantly. The calculated frequencies are an average of 3.7% higher than experiment at the MP2/6-31G(*d*) level, and 1.9% higher at the MP2/6-311 + G(*d,p*) level. The estimated MP2/6-311 + + G(3*d,3p*) frequencies are in very good agreement with the experimental harmonic values averaging only 1.25% too high. The largest discrepancies are for the CH stretching modes; this may be due to the large anharmonicity of the CH stretch and the empirical method of estimating the experimental harmonic frequencies.⁹

IR intensities

The calculated and experimental intensities are summarized in Table IV; selected calculations are compared to experimental values in Fig. 2. Augmenting the split valence (6-31G) and triple split valence (6-311G) basis sets with diffuse functions on the carbon and fluorine atoms decreases the intensities of the CH_2 vibrational modes while it increases the intensities of the CF_2 vibrational modes. The inclusion of diffuse functions on the hydrogen atoms has very little effect on the intensities of any of the modes. The addition of one set of *d* polarization functions on the heavy atoms in general increases the intensities of the CH_2 modes and the CF_2 stretching modes. However, the CF_2 bending

TABLE IV. Calculated and experimental IR absorption intensities (kilometers per mole).

Calculational level	$A_1 \nu_1$ CH sym stretch	$A_1 \nu_2$ CH ₂ scissor	$A_1 \nu_3$ CF sym stretch	$A_1 \nu_4$ CF ₂ bend	$B_1 \nu_6$ CH as stretch	$B_1 \nu_7$ CH ₂ rock	$B_2 \nu_8$ CH ₂ wag	$B_2 \nu_9$ CF as stretch	$\nu_1 + \nu_6^a$ integrated intensity	$\nu_3 + \nu_7 + \nu_9^a$ integrated intensity
HF/STO-3G	8.33	3.07	21.32	8.31	8.45	24.08	49.05	11.44	16.78	56.84
HF/3-21G	43.24	7.47	110.23	13.88	75.98	33.17	58.88	154.43	119.22	297.83
HF/4-31G	34.95	4.02	122.92	15.92	55.70	31.53	43.24	199.49	90.65	353.94
HF/6-31G	36.06	3.66	124.17	16.12	52.83	32.07	49.41	203.46	88.89	359.70
HF/6-31G(<i>d</i>)	47.62	7.91	136.41	6.04	70.68	31.09	53.96	249.44	118.30	416.94
HF/6-31G(2 <i>d</i>)	39.96	3.39	122.68	4.47	52.19	26.74	32.37	239.27	92.15	388.69
HF/6-31G(3 <i>d</i>)	42.07	2.00	128.14	5.66	38.94	26.36	28.08	269.83	81.01	424.33
HF/6-31 + G	30.47	1.40	128.40	18.00	31.92	29.67	37.82	241.69	62.39	399.76
HF/6-31 + G(<i>d</i>)	44.20	4.76	143.58	6.91	45.59	28.42	42.15	299.14	89.79	471.14
HF/6-31 + G(<i>d,p</i>)	45.67	3.41	143.49	6.86	43.04	27.68	36.01	299.32	88.71	470.49
HF/6-31 + G(<i>d,2p</i>)	46.76	2.55	141.53	6.82	41.57	26.56	29.69	295.65	88.33	463.74
HF/6-31 + + G(<i>d,2p</i>)	47.16	2.33	141.72	6.77	41.87	26.07	30.48	295.59	89.03	463.38
HF/6-31 + G(<i>d,3p</i>)	45.17	1.34	137.85	6.59	37.52	25.94	22.69	290.10	82.69	453.89
HF/6-31 + G(2 <i>d,p</i>)	41.03	1.22	132.72	5.10	35.25	23.62	20.36	288.10	76.28	444.44
HF/6-31 + G(3 <i>d,p</i>)	43.11	0.82	132.81	5.55	34.50	24.42	19.71	288.08	77.61	445.31
HF/6-311G	40.51	2.40	126.69	15.05	44.60	35.66	50.30	222.14	85.11	384.49
HF/6-311G(<i>d</i>)	53.58	4.62	151.01	6.08	63.64	34.29	46.11	285.46	117.22	470.76
HF/6-311G(<i>d,p</i>)	48.22	3.29	148.59	6.27	54.40	32.88	40.14	280.94	102.62	462.41
HF/6-311 + G	37.44	0.87	129.12	16.10	36.83	30.56	40.82	244.76	74.27	404.44
HF/6-311 + G(<i>d</i>)	50.36	3.00	152.94	6.55	49.47	29.18	36.14	314.71	99.83	496.83
HF/6-311 + G(<i>d,p</i>)	47.12	1.97	150.83	6.70	44.08	27.91	31.51	310.77	91.20	489.51
HF/6-311 + + G(<i>d,p</i>)	47.87	1.94	150.94	6.65	43.66	27.87	32.31	310.39	91.53	489.20
HF/6-311 + + G(2 <i>d,p</i>)	42.22	1.40	138.83	5.57	35.47	25.60	22.89	293.13	77.69	457.56
HF/6-311 + + G(2 <i>dd',p</i>)	42.33	1.12	135.82	5.48	34.19	24.45	19.82	290.17	76.52	450.44
HF/6-311 + + G(3 <i>d,p</i>)	43.75	1.14	131.43	5.12	35.97	23.54	19.54	282.90	79.72	437.87
MP2/6-31G(<i>d</i>)	46.60	5.22	99.79	5.85	62.38	21.60	52.39	200.58	108.98	321.97
MP2/6-311 + G(<i>d,p</i>)	46.21	1.62	113.41	6.36	37.85	20.16	29.66	274.57	84.06	408.14
est MP2/6-311 + + G(3 <i>d,p</i>)	42.84	0.79	94.01	4.78	29.74	15.79	17.69	246.70	72.60	356.50
est MP2/6-311 + + G(3 <i>d,3p</i>)	42.34	(-1.28)	88.37	4.51	24.22	14.05	4.37	237.48	66.56	339.90
Experimental ^{b,c}	22.40	d	89.50	4.80	42.20	14.40	10.30	230.40	64.60	333.90
Experimental ^e	29.80	d	54.99	4.70	41.00	8.95	10.34	243.94	69.43	307.88
Experimental ^f	23.60	d	66.34	4.97	42.21	0.04	10.58	294.30	65.81	334.30
Experimental ^g								316.39		

^a Bands 1 and 6 overlap and bands 3, 7, and 9 overlap.

^b ν_2 is symmetry forbidden.

^c See Ref. 2.

^d Below detection limit.

^e See Ref. 8.

^f See Ref. 7.

^g See Ref. 1.

mode intensity is reduced by nearly a factor of 3, bringing it closer to the experimental values. A second set of *d* functions slightly decreases the intensities of all of the modes and a third set has a relatively small effect on all of the modes. The addition of one set of *p* polarization functions to the hydrogen atoms decreases the intensity of the CH₂ symmetric and asymmetric stretching, and wag modes. A second and third set of *p* functions also significantly decreases the intensities of these modes, but not the other modes. At the HF/6-311 + + G(3*d,p*) level the average absolute error is 17.7 kilometers per mole with the largest errors in the CF₂ stretching modes and the CH₂ symmetric stretch. Correlation corrections at the MP2 level with both the 6-31G(*d*) and 6-311 + G(*d,p*) basis sets decrease the intensity of all modes. By far the largest effect is for the CF stretching modes. Basis set effects and correlation corrections can be combined according Eqs. (3) and (4) to yield estimated MP2/6-311 + + G(3*d,p*) and MP2/6-311 + + G(3*d,3p*)

intensities. A comparison of the calculated and estimated intensities at the MP2/6-311 + G(*d,p*) level [see Eq. (2)] indicates that the errors in the estimation process are less than ± 3 km/mol or $\pm 5\%$ (whichever is higher).

Direct comparison of the intensities with experiment is hampered by extensive overlap between ν_1 and ν_6 and between ν_3 , ν_7 , and ν_9 . To avoid any uncertainties arising from the deconvolution of the overlapping bands the calculations are compared to the sums of the intensities of these bands. At the HF/6-311 + G(*d,p*) level, the average error for A_2 , A_4 , A_8 , $A_1 + A_6$, and $A_3 + A_7 + A_9$ is 41 km/mol; correlation corrections reduce the error to 23 km/mol, primarily by improving the value for $A_3 + A_7 + A_9$. Improvements in the basis yield an average error of 26 km/mol at the HF/6-311 + + G(3*d,p*) level. Combining the basis set and correlation effects reduces the average error to 7.8 km/mol at the est MP2/6-311 + + G(3*d,p*) level and 3.1 km/mol at the MP2/6-311 + + G(3*d,3p*) level relative to the best esti-

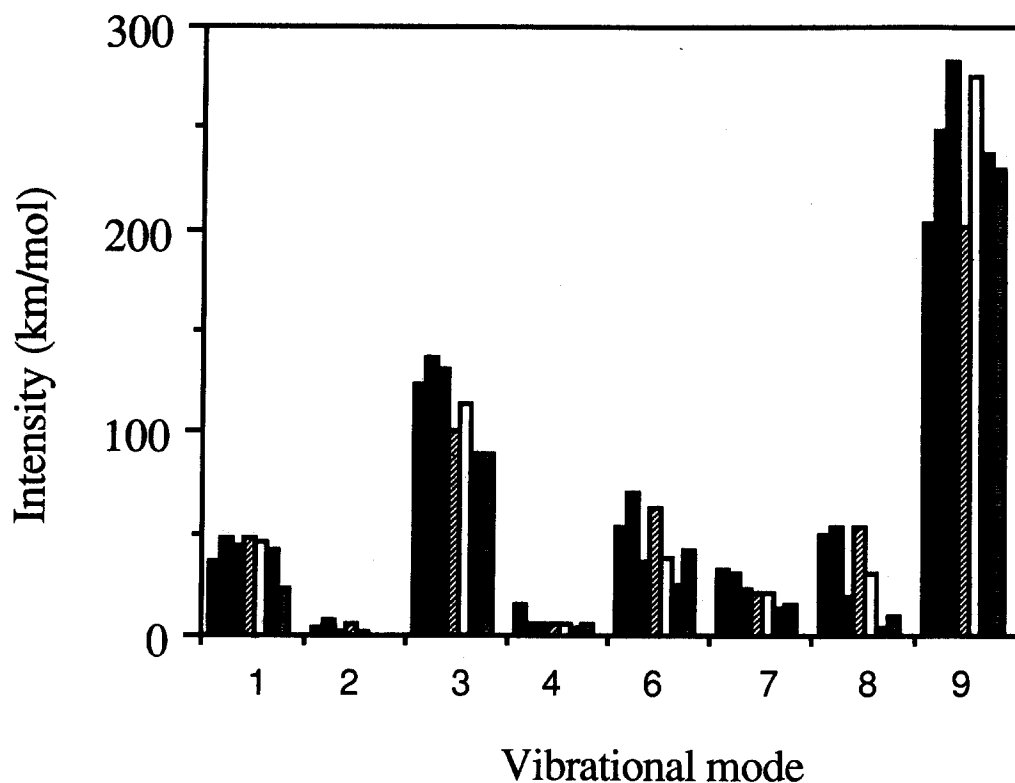


FIG. 2. Calculated and experimental IR absorption intensities for CH₂F₂. From left to right for each mode: HF/6-31G, HF/6-31G(d), HF/6-311 + G(3d,p), MP2/6-31G(d), MP2/6-311 + G(d,p), estimated MP2/6-311 + G(3d,3p), and experimental.²

mate of the experimental intensities.²

Even though the sum of the calculated intensities of the overlapping CH stretching bands (ν_1 and ν_6) agrees well with experiment, there are sizeable differences when considering them separately. The origin of this discrepancy is unclear; however, a similar problem occurs in CH₂O.^{13,20} The addition of an extra set of diffuse polarization functions, i.e., the HF/6-311 + G(2dd',p)¹³ entries in the tables, results in only very minor changes in the intensities; perhaps higher levels of electron correlation might improve the agreement.¹³ On the other hand, the problems with ν_1 and ν_6 may be the result of electrical anharmonicity and mechanical anharmonicity. Alternatively this may be due to a Fermi resonance between ν_1 and $2\nu_2$ that has been identified for methylene fluoride and similar molecules.²¹ The ν_3 and ν_9 bands may be subject to similar difficulties.

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