

# A theoretical study of the infrared vibrational intensities of CH<sub>3</sub>F

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The atomic polar tensors, vibrational frequencies, and infrared intensities were calculated for methyl fluoride using *ab initio* molecular orbital methods. Calculations were carried out using several split-valence basis sets (3-21G, D95, 6-31G, 6-311G) augmented with various numbers of diffuse and polarization functions. The CID/6-31G(*d*) optimized geometry was found to agree well with the experimental geometry and was used for all of the calculations. Atomic polar tensors were computed by analytical differentiation of the dipole moment at the Hartree-Fock level, and by numerical differentiation at the CISD level. The Hartree-Fock limit of the dipole moment is estimated to be  $2.06 \pm 0.02$  D at the CID/6-31G(*d*) optimized geometry. Compared with the observed, anharmonic vibrational frequencies, the calculated frequencies are an average of  $8 \pm 4\%$  too high at the HF/6-311 + + G(3*d*,3*p*) level, with larger errors for bending modes than for stretches. When correlation corrections are included the errors are significantly smaller and more uniform,  $4.4 \pm 1.0\%$ . Infrared intensities are much more sensitive to basis set effects than frequencies, requiring multiple sets of polarization functions, diffuse functions, and correlation corrections. A useful relation has been found between the calculated molecular dipole moment and the intensity of the CF stretching mode.

## INTRODUCTION

Although a number of groups have studied the experimental infrared vibrational intensities of CH<sub>3</sub>F, there are still significant differences in the values reported for some bands. For the  $\nu_3$  band, Arimondo and Oka<sup>1</sup> have estimated a transition dipole of 0.144 D, whereas Barrow and McKean<sup>2</sup> obtained 0.195 D from integrated band intensities. Intensity data from other groups<sup>3,4</sup> correspond to a transition dipole of  $\sim 0.18$  D for  $\nu_3$ . More recently, Adam, Gough, Isenor, and Scoles<sup>5</sup> have measured a rotationless transition dipole moment of 0.21 D for the  $\nu_3$  fundamental, based on Rabi oscillations in molecular beam, laser-Stark spectroscopy.

Absolute infrared intensities and transition dipole moments are usually interpreted in terms of atomic polar tensors,<sup>5-9</sup> i.e., derivatives of the dipole moment with respect to the Cartesian coordinates. Often there is considerable ambiguity in fitting the atomic polar tensors to the observed intensities. For many molecules, even after extensive studies, it may be difficult to choose the correct combination of signs for the dipole moment derivatives based on the experimental data alone. Theoretical calculations can help resolve some of these difficulties. Person and co-workers<sup>10,11</sup> have calculated the infrared intensities of methyl fluoride by semiempirical methods at the CNDO level and by *ab initio* methods at the HF/4-31G level. Lakdar, Taillander, and Berthier<sup>12</sup> have used *ab initio* calculations at the SCF level with double-zeta basis sets augmented with polarization functions to obtain the dipole moment derivatives of CH<sub>3</sub>F. These calculations agree on the sign of the dipole moment derivatives, but still larger calculations are needed for good agreement with experimental infrared intensities.

In theoretical calculations, the atomic polar tensors or dipole moment derivatives can be calculated by numerical differentiation using the dipole moment computed at the equilibrium geometry and at the small displacements of each atom along the coordinate axes. The dipole moment derivatives can also be calculated numerically by determining the change in the analytical energy gradient (with respect to the atom positions) under the influence of a finite external electric field.<sup>13</sup> Alternatively, the dipole moment derivatives can be calculated analytically.<sup>14-16</sup>

Dipole moments are difficult to compute accurately, usually requiring rather large basis sets and correlation corrections. Similar difficulties are encountered in the computation of dipole moment derivatives and infrared intensities.<sup>15,16</sup> In the present study on the infrared intensities of methyl fluoride, we have explored the effects of basis sets and correlation corrections on the dipole moment, atomic polar tensors, vibrational frequencies, and infrared intensities of methyl fluoride.

## METHOD

*Ab initio* molecular orbital calculations were performed with the GAUSSIAN 82 system of programs.<sup>17</sup> The equilibrium geometries were obtained from the literature.<sup>18,19</sup> Vibrational frequencies were computed using analytical second derivatives<sup>20</sup> at the Hartree-Fock level with STO-3G, 3-21G, 4-31G, 6-31G, 6-31G, 6-311G basis sets<sup>21</sup> and Huzinaga's<sup>22</sup> 9s5*p* basis set using Dunning's [4s2*p*] contraction,<sup>23</sup> designated D95 in the tables. The larger basis sets were also augmented with several sets of polarization functions and diffuse functions.

At the SCF level, the derivatives of the dipole moment with respect to the Cartesian coordinates of the nuclei can be computed analytically:

<sup>a)</sup> Camille and Henry Dreyfus Teacher-Scholar.

$$\frac{\partial \mu_a}{\partial \beta_A} = \sum_{\mu\nu} \left[ \frac{\partial P_{\mu\nu}}{\partial \beta_A} \langle \nu | \alpha | \mu \rangle + P_{\mu\nu} \frac{\partial \langle \rho | \alpha | \mu \rangle}{\partial \beta_A} \right] + \sum_A \alpha_A Z_A, \quad (1)$$

where  $P_{\mu\nu}$  are the density matrix elements,  $\langle \nu | \alpha | \mu \rangle$  are the dipole moment integrals, and  $\alpha, \beta$  are the Cartesian directions  $x, y,$  and  $z$ ; subscript  $A$  indicates the Cartesian coordinates referred to center  $A$ . The derivatives of  $P_{\mu\nu}$  are obtained by solving the CPHF equations.<sup>14,20</sup> At the CISD (frozen core) level the dipole moment is computed as the expectation value of  $\mu$ . This has been shown to be in close agreement with the dipole calculated as the derivative of the CI energy with respect to the electric field.<sup>24</sup> Dipole moment derivatives at the CISD level (configuration interaction with all single and double excitations) were computed numerically by forward difference with a step size of 0.02 Å.

For the orientation given in Fig. 1, the atomic polar tensor for CH<sub>3</sub>F can be written as

$$P^A = \begin{bmatrix} a_A & 0 & 0 \\ 0 & a_A & 0 \\ 0 & 0 & b_A \end{bmatrix}, \quad P^H = \begin{bmatrix} a_H & 0 & 0 \\ 0 & b_H & d_H \\ 0 & e_H & c_H \end{bmatrix}, \quad (2)$$

where  $A = C, F$ . Because of the dependence on the orientation of the molecule, direct comparisons of the atomic polar tensors are inconvenient. A number of rotationally invariant components can be obtained from the atomic polar tensor.<sup>25-27</sup> In terms of Eq. (2) the absolute effective atomic charge for  $P^H$  is

$$|\chi_H| = \frac{1}{3^{1/2}} (a_H^2 + b_H^2 + c_H^2 + d_H^2 + e_H^2)^{1/2}. \quad (3)$$

The mean dipole derivative<sup>25-27</sup> can be expressed as

$$\bar{\mu}_H = 1/3 (a_H + b_H + c_H) \quad (4)$$

and the anisotropy<sup>25-27</sup> is

$$\beta_H^2 = 1/2 [(a_H - b_H)^2 + (b_H - c_H)^2 + (c_H - a_H)^2 + 3(d_H^2 + e_H^2)]. \quad (5)$$

After the atomic polar tensors have been transformed from Cartesian coordinates to normal modes,  $Q_i$ , the absolute infrared intensities can be computed in the harmonic approximation<sup>28</sup> by

$$A_i = \frac{N\pi d_i}{3c^2} \left| \frac{\partial \mu}{\partial Q_i} \right|^2,$$

where  $N$  is Avogadro's number,  $d_i$  is the degeneracy of the

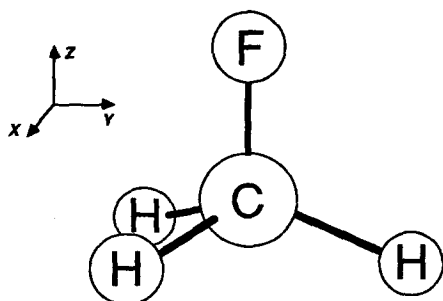


FIG. 1. Orientation of methyl fluoride used in the calculations.

$i$ th fundamental, and  $c$  is the velocity of light. The absolute infrared intensities are given in km/mol.<sup>7</sup>

## RESULTS AND DISCUSSION

### Geometry

The experimental and theoretical geometries for methyl fluoride are collected in Table I. Since the effects of basis sets and electron correlation on theoretical equilibrium geometries have been discussed previously,<sup>18</sup> only a brief summary is given here. Computed structures at the Hartree-Fock level without polarization functions overestimate the C-F bond length by approximately 0.03 Å and underestimate the C-H bond length by 0.01 Å compared to the experiment. The addition of polarization functions to the basis set improves the C-H bond length, but the C-F distance is underestimated by ~0.03 Å. Inclusion of correlation energy at the CID/6-31G( $d$ ) level [configuration interaction with all double excitations using the 6-31G( $d$ ) basis set] leads to very good agreement with the experimental results. The C-F bond length is closer to the value reported by Duncan, McKean, and Spies,<sup>29</sup> but the HCF angle agrees slightly better with the value obtained by Blom and Muller.<sup>30</sup> As suggested by Pulay<sup>31</sup> we have separated the basis set effect on geometry from the basis set effect on the dipole moment, infrared intensities, and vibrational frequencies, by using the best theoretical geometry [CID/6-31G( $d$ )] for the remainder of the calculations.

### Dipole moment

The total energies and dipole moments computed at the CID/6-31( $d$ ) optimized geometry with a variety of basis sets are collected in Table II. Jaquet, Kutzelnigg, and Staemmler<sup>32</sup> pointed out that if the energy is good enough with one set of polarization functions the dipole moment requires two or three sets of polarization functions. This can be confirmed by inspecting the data in Table II and in Figs. 2 and 3, which compare the rate of convergence of the energy and the dipole moment.

TABLE I. Optimized geometries of methyl fluoride.<sup>a</sup>

Method	$R(\text{CF})$	$R(\text{CH})$	$\langle \text{HCF} \rangle$
HF/STO-3G	1.384	1.097	110.6
HF/3-21G	1.404	1.080	109.4
HF/4-31G	1.412	1.076	108.3
HF/6-21G	1.408	1.080	109.4
HF/6-31G	1.415	1.077	108.2
HF/6-31G( $d$ )	1.365	1.082	109.1
HF/6-311G( $d$ )	1.362	1.081	108.9
CID/6-31G( $d$ )	1.382	1.090	109.1
Experiment <sup>b</sup>	1.389	1.084	108.6
Experiment <sup>c</sup>	1.382	1.095	108.4

<sup>a</sup> See Refs. 18 and 19.

<sup>b</sup> See Ref. 30.

<sup>c</sup> See Ref. 29.

TABLE II. Calculated total energies and dipole moments.<sup>a</sup>

Basis set	(Primitives)/[Contraction]	Primitive functions	Contracted functions	<i>E</i> (a.u.)	<i>μ</i> (D)
HF level					
STO-3G	(6s,3p/3s)/[2s,1p/1s]	39	13	-137.168 48	1.157
3-21G	(6s,3p/3s)/[3s,2p/2s]	39	24	-138.281 25	2.252
6-21G	(9s,3p/3s)/[3s,2p/2s]	45	24	-138.835 46	2.223
4-31G	(8s,4p/4s)/[3s,2p/2s]	52	24	-138.857 69	2.499
D95	(9s,5p/4s)/[3s,2p/2s]	60	26	-139.030 35	2.598
D95( <i>d</i> )	(9s,5p,1d/4s)/[3s,2p,1d/2s]	72	38	-139.074 00	2.178
6-31G	(10s,4p/4s)/[3s,2p/2s]	56	24	-138.993 34	2.500
6-31 + G	(11s,5p/4s)/[4s,3p/2s]	64	32	-139.002 00	2.655
6-31 + + G	(11s,5p/5s)/[4s,3p/3s]	67	35	-139.002 02	2.655
6-31G( <i>d</i> )	(10s,4p,1d/4s)/[3s,2p,1d/2s]	68	36	-139.034 21	2.065
6-31G(2 <i>d</i> )	(10s,4p,2d/4s)/[3s,2p,2d/2s]	80	48	-139.035 38	1.936
6-31G(3 <i>d</i> )	(10s,4p,3d/4s)/[3s,2p,3d/2s]	92	60	-139.044 09	1.987
6-31G( <i>d,p</i> )	(10s,4p,1d/4s,1p)/[3s,2p,1d/2s,1p]	77	45	-139.039 38	2.057
6-31G(2 <i>d</i> ,2 <i>p</i> )	(10s,4p,2d/4s,2p)/[3s,2p,2d/2s,2p]	98	66	-139.042 06	1.939
6-31 + G( <i>d</i> )	(11s,5p,1d/4s)/[4s,3p,1d/2s]	76	44	-139.043 85	2.232
6-31 + G(2 <i>d</i> )	(11s,5p,2d/4s)/[4s,3p,2d/2s]	88	56	-139.045 63	2.071
6-31 + G(3 <i>d</i> )	(11s,5p,3d/4s)/[4s,3p,3d/2s]	100	68	-139.048 89	2.039
6-31 + + G( <i>d,p</i> )	(11s,5p,1d/5s,1p)/[4s,3p,1d/3s,1p]	88	56	-139.048 84	2.234
6-31 + + G(2 <i>d</i> ,2 <i>p</i> )	(11s,5p,2d/5s,2p)/[4s,3p,2d/3s,2p]	109	77	-139.051 95	2.087
6-31 + + G(3 <i>d</i> ,3 <i>p</i> )	(11s,5p,3d/5s,3p)/[4s,3p,3d/3s,3p]	130	98	-139.054 48	2.052
6-311G	(11s,5p/5s)/[4s,3p/3s]	67	35	-139.034 89	2.510
6-311 + G	(12s,6p/5s)/[5s,4p/3s]	75	43	-139.039 00	2.590
6-311 + + G	(12s,6p/6s)/[5s,4p/4s]	78	46	-139.039 00	2.591
6-311G( <i>d</i> )	(11s,5p,1d/5s)/[4s,3p,1d/3s]	77	45	-139.072 36	2.171
6-311G(2 <i>d</i> )	(11s,5p,2d/5s)/[4s,3p,2d/3s]	87	55	-139.075 63	2.009
6-311G(3 <i>d</i> )	(11s,5p,3d/5s)/[4s,3p,3d/3s]	97	65	-139.079 29	1.877
6-311 + + G( <i>d</i> )	(12s,6p,1d/6s)/[5s,4p,1d/4s]	88	56	-139.078 11	2.245
6-311 + + G(2 <i>d</i> )	(12s,6p,2d/6s)/[5s,4p,2d/4s]	98	66	-139.080 49	2.084
6-311 + + G(3 <i>d</i> )	(12s,6p,3d/6s)/[5s,4p,3d/4s]	108	76	-139.083 06	2.046
6-311G( <i>d,p</i> )	(11s,5p,1d/5s,1p)/[4s,3p,1d/3s,1p]	86	54	-139.077 80	2.154
6-311 + G( <i>d,p</i> )	(12s,6p,1d/5s,1p)/[5s,4p,1d/3s,1p]	94	62	-139.082 75	2.237
6-311 + G(2 <i>d,p</i> )	(12s,6p,2d/5s,1p)/[5s,4p,2d/3s,1p]	104	72	-139.085 94	2.112
6-311 + G(2 <i>d</i> , <i>f</i> )	(12s,6p,2d,1f/5s,1p)/[5s,4p,2d,1f/3s,1p]	118	86	-139.089 32	2.101
6-311 + + G( <i>d,p</i> )	(12s,6p,1d/6s,1p)/[5s,4p,1d/4s,1p]	97	65	-139.082 82	2.238
6-311 + + G(2 <i>d,p</i> )	(12s,6p,2d/6s,1p)/[5s,4p,2d/4s,1p]	107	75	-139.086 01	2.112
6-311 + + G(3 <i>d,p</i> )	(12s,6p,3d/6s,1p)/[5s,4p,3d/4s,1p]	117	85	-139.087 54	2.060
6-311 + + G(2 <i>d</i> ,2 <i>p</i> )	(12s,6p,2d/6s,2p)/[5s,4p,2d/4s,2p]	116	84	-139.087 37	2.113
6-311 + + G(3 <i>d</i> ,3 <i>p</i> )	(12s,6p,3d/6s,3p)/[5s,4p,3d/4s,3p]	135	103	-139.089 03	2.063
6-311 + + G(3 <i>d</i> , <i>f</i> ,3 <i>p</i> )	(12s,6p,3d,1f/6s,3p)/[5s,4p,3d,1f/4s,3p]	149	117	-139.092 36	2.060
Estimated HF limit					2.06 ± 0.02
CISD level					
3-21G	(6s,3p/3s)/[3s,2p/2s]	39	24	-139.505 89	1.967
6-31G( <i>d</i> )	(10s,4p,1d/4s)/[3s,2p,1d/2s]	68	36	-139.354 78	1.897
6-31G(2 <i>d</i> )	(10s,4p,2d/4s)/[3s,2p,2d/2s]	80	48	-139.398 33	1.794
6-31 + G(2 <i>d</i> )	(11s,5p,2d/4s)/[4s,3p,2d/2s]	88	56	-139.414 11	1.971
Experiment <sup>b</sup>					1.856

<sup>a</sup>All calculations were performed at the CID/6-31G(*d*) optimized geometry.<sup>b</sup>See Ref. 1(a).

The difference in the dipole moment between the 6-31G and 6-311G basis set is small and similar trends are observed when both basis sets are augmented with diffuse functions and/or polarization functions. The addition of diffuse functions to hydrogen is relatively unimportant, but diffuse functions on heavy atoms increase the dipole moment by 0.08–0.18 D. Enlarging the basis sets with one set of polarization functions on heavy atoms decreases the dipole moment by 0.3–0.5 D. Polarization functions on hydrogen have only a

very small effect since the dipole moment is dominated by the polarity of the C–F bond. A second and third set of polarization functions on the heavy atoms improves the dipole moment by ~0.1–0.2 D. A comparison of the dipole moment computed with the 6-311 + + G(3*d*,3*p*) and 6-311 + + G(3*d*,*f*,3*p*) basis sets shows that *f* functions change the dipole moment by less than 0.01 D at the CID/6-31G(*d*) optimized geometry. This suggests that the Hartree–Fock limit is  $\mu = 2.06 \pm 0.02$  D. Correlation correc-

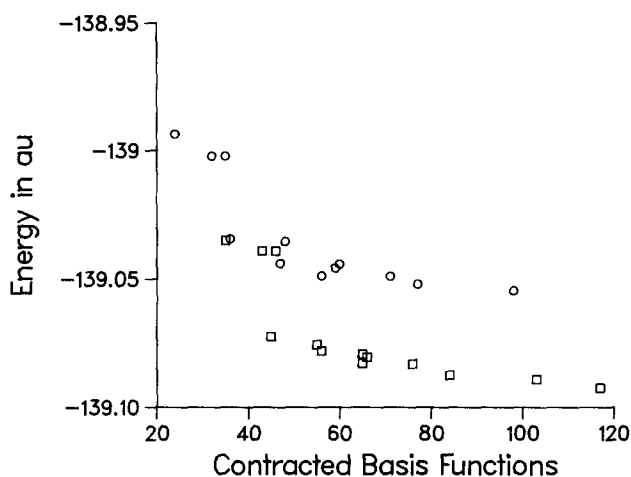


FIG. 2. Methyl fluoride total energy as a function of the number of contracted basis functions. (Circles: 6-31G with diffuse and polarization functions; squares 6-311G with diffuse and polarization functions.)

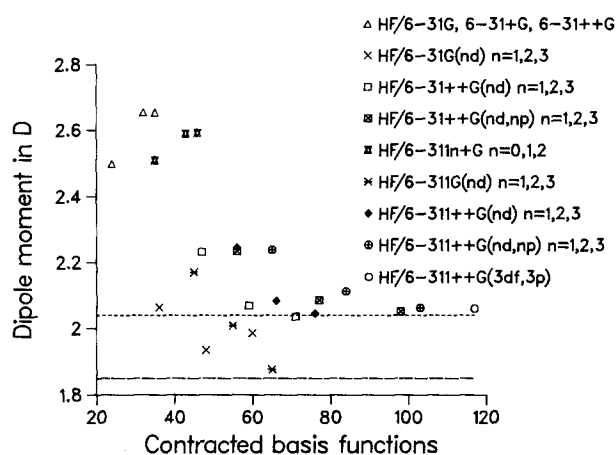


FIG. 3. Methyl fluoride dipole moment as a function of the number of contracted basis functions. The dashed line corresponds to the experimental dipole moment and the dotted line is the estimated Hartree-Fock limit.

tions to the calculated dipole moment are quite significant. Inclusion of all single and double excitations lowers the dipole by 0.17, 0.14, and 0.10 D with the 6-31G(*d*), 6-31G(2*d*), and 6-31 + G(2*d*) basis sets, respectively.

### Atomic polar tensors

Table III summarizes the atomic polar tensors for various basis sets; the trends are quite similar to the dipole mo-

TABLE III. Calculated atomic polar tensors.<sup>a</sup>

Basis set	Carbon		Fluorine		Hydrogen				
	$a_C$	$b_C$	$a_F$	$b_F$	$a_H$	$b_H$	$c_H$	$d_H$	$e_H$
HF level									
STO-3G	0.236	0.289	-0.209	-0.258	0.025	-0.043	-0.010	0.020	-0.025
3-21G	0.488	0.835	-0.330	-0.762	0.052	-0.157	-0.024	0.057	0.045
4-31G	0.461	0.926	-0.377	-0.877	0.074	-0.130	-0.016	0.057	0.030
6-21G	0.465	0.893	-0.376	-0.849	0.073	-0.132	-0.015	0.056	0.031
D95	0.530	1.060	-0.387	-1.015	0.084	-0.179	-0.015	0.096	0.037
D95( <i>d</i> )	0.536	1.203	-0.342	-1.107	0.048	-0.178	-0.032	0.088	0.033
6-31G	0.496	0.948	-0.370	-0.897	0.067	-0.151	-0.017	0.062	0.035
6-31 + G	0.473	1.009	-0.399	-0.982	0.082	-0.132	-0.009	0.074	0.018
6-31 + + G	0.475	1.011	-0.398	-0.981	0.084	-0.135	-0.010	0.074	0.020
6-31G( <i>d</i> )	0.522	1.103	-0.324	-1.006	0.036	-0.168	-0.034	0.068	0.034
6-31G(2 <i>d</i> )	0.469	1.039	-0.309	-0.978	0.041	-0.147	-0.020	0.065	0.021
6-31G(3 <i>d</i> )	0.458	1.091	-0.325	-1.037	0.053	-0.142	-0.018	0.076	0.008
6-31G( <i>d,p</i> )	0.511	1.091	-0.321	-1.007	0.040	-0.166	-0.028	0.071	0.034
6-31G(2 <i>d</i> ,2 <i>p</i> )	0.473	1.025	-0.304	-0.977	0.044	-0.158	-0.016	0.076	0.029
6-31 + G( <i>d,p</i> )	0.487	1.172	-0.350	-1.108	0.057	-0.148	-0.021	0.084	0.020
6-31 + + G( <i>d,p</i> )	0.485	1.175	-0.349	-1.109	0.058	-0.149	-0.022	0.084	0.020
6-311G	0.517	1.011	-0.383	-0.943	0.072	-0.161	-0.023	0.070	0.026
6-311 + + G	0.495	1.039	-0.394	-0.990	0.081	-0.149	-0.017	0.077	0.020
6-311G( <i>d</i> )	0.535	1.145	-0.344	-1.069	0.051	-0.177	-0.025	0.076	0.028
6-311G( <i>d,p</i> )	0.504	1.120	-0.340	-1.062	0.055	-0.164	-0.019	0.073	0.024
6-311 + G( <i>d,p</i> )	0.481	1.174	-0.352	-1.126	0.065	-0.151	-0.016	0.082	0.016
6-311 + + G( <i>d,p</i> )	0.483	1.175	-0.352	-1.126	0.064	-0.151	-0.016	0.082	0.017
6-311 + + G(2 <i>d</i> , <i>p</i> )	0.456	1.127	-0.336	-1.097	0.062	-0.143	-0.010	0.082	0.012
6-311 + + G(3 <i>d</i> , <i>p</i> )	0.447	1.105	-0.327	-1.073	0.063	-0.143	-0.011	0.086	0.013
6-311 + + G(2 <i>d</i> ,2 <i>p</i> )	0.453	1.122	-0.335	-1.092	0.064	-0.143	-0.010	0.083	0.013
6-311 + + G(3 <i>d</i> ,3 <i>p</i> )	0.441	1.101	-0.326	-1.078	0.065	-0.142	-0.008	0.088	0.013
CIDSD level									
3-21G	0.488	0.835	-0.330	-0.762	0.052	-0.157	-0.024	0.057	0.045
6-31G( <i>d</i> )	0.431	1.009	-0.282	-0.903	0.047	-0.153	-0.035	0.078	0.042

<sup>a</sup> Atomic polar tensors in a.u. All computations at the CID/6-31G(*d*) optimized geometry; see Eqs. (2) and (3) for notation.

ment. Diffuse functions on the heavy atoms do affect the derivatives of the dipole moment, but diffuse functions on hydrogen do not. This has also been noticed for HCN molecule.<sup>33</sup> One set of polarization functions on heavy atoms overestimates the derivatives of the dipole moment. A second set of polarization functions appears to be rather important for all the elements of the atomic polar tensors. Polarization functions on hydrogen are important for the  $P^H$  atomic polar tensor but not for  $P^C$  or  $P^F$ . A number of components of the atomic polar tensors are quite sensitive to electron correlation corrections.

The components of the atomic polar tensor depend on the orientation of the molecule, making comparisons with experiment and with other calculations somewhat difficult. These problems can be circumvented if comparisons are based on the rotational invariants, e.g., effective charge, mean dipole, and anisotropy.<sup>25-27</sup> Table IV summarizes the calculated and experimental rotational invariants of the atomic polar tensors. Surprisingly good agreement with the experimental results is obtained with the split-valence basis sets. However, the values change as the basis set is enlarged, indicating that the good agreement of the split-valence is due

to cancellation between basis set errors and correlation effects. Similar to the dipole moment, the rotational invariants are affected significantly by correlation corrections.

### Vibrational frequencies

The calculated and experimental vibrational frequencies are collected in Table V; selected values are plotted in Fig. 4. All of the split-valence calculations are very similar. More extensive studies<sup>20,34,35</sup> indicate that harmonic frequencies at this level of calculation are typically 10%–15% too high when compared to experiment primarily due to vibrational anharmonicity and electron correlation effects. As pointed out previously, there are also significant basis set effects.<sup>16,31</sup> A set of  $d$  orbitals on the heavy atoms lowers the C–F stretch by as much as 80 cm<sup>-1</sup> and raises the C–H stretch modes by up to 45 cm<sup>-1</sup>. A second set of  $d$  functions can also shift the frequencies significantly. A set of  $p$  functions on the hydrogens lowers some modes by more than 20 cm<sup>-1</sup>; a second set seems to be less important. When added to a polarized basis, diffuse functions on heavy atoms lower the frequencies by another 0–10 cm<sup>-1</sup> while diffuse functions on hydrogen have almost no effect. A change from a

TABLE IV. Calculated and experimental invariants of the atomic polar tensors for CH<sub>3</sub>F.<sup>a</sup>

Basis set	$\chi_F$	$\chi_C$	$\chi_H$	$\mu_F$	$\mu_C$	$\mu_H$	$\beta_F^2$	$\beta_C^2$	$\beta_H^2$
HF level									
STO-3G	0.227	0.255	0.035	-0.225	0.254	-0.010	0.002	0.003	0.005
3-21G	0.516	0.625	0.106	-0.474	0.604	-0.043	0.187	0.120	0.042
4-31G	0.586	0.668	0.104	-0.537	0.639	-0.034	0.251	0.174	0.044
6-21G	0.511	0.630	0.109	-0.469	0.609	-0.047	0.185	0.115	0.044
D95	0.666	0.750	0.129	-0.596	0.707	-0.037	0.394	0.281	0.069
D95( $d$ )	0.697	0.821	0.121	-0.597	0.758	-0.054	0.585	0.445	0.053
6-31G	0.600	0.681	0.104	-0.546	0.646	-0.034	0.278	0.204	0.044
6-31 + G	0.654	0.699	0.100	-0.593	0.652	-0.020	0.341	0.287	0.043
6-31 + + G	0.653	0.700	0.102	-0.592	0.653	-0.020	0.340	0.287	0.045
6-31G( $d$ )	0.638	0.766	0.110	-0.551	0.716	-0.055	0.466	0.337	0.041
6-31G( $2d$ )	0.619	0.711	0.097	-0.532	0.659	-0.042	0.447	0.325	0.035
6-31G( $3d$ )	0.655	0.733	0.099	-0.562	0.669	-0.036	0.507	0.401	0.038
6-31G( $d,p$ )	0.638	0.756	0.111	-0.550	0.704	-0.052	0.471	0.337	0.044
6-31G( $2d,2p$ )	0.616	0.707	0.106	-0.528	0.657	-0.043	0.454	0.305	0.042
6-31 + G( $d,p$ )	0.701	0.785	0.105	-0.603	0.715	-0.038	0.575	0.470	0.043
6-31 + + G( $d,p$ )	0.701	0.786	0.106	-0.602	0.715	-0.038	0.578	0.475	0.044
6-311G	0.628	0.517	0.111	-0.570	0.681	-0.037	0.313	0.244	0.049
6-311 + + G	0.656	0.724	0.109	-0.592	0.677	-0.028	0.355	0.294	0.050
6-311G( $d$ )	0.678	0.792	0.117	-0.586	0.738	-0.051	0.525	0.372	0.050
6-311G( $d,p$ )	0.673	0.767	0.110	-0.581	0.709	-0.043	0.520	0.379	0.046
6-311 + G( $d,p$ )	0.711	0.783	0.107	-0.610	0.712	-0.034	0.600	0.480	0.046
6-311 + + G( $d,p$ )	0.711	0.784	0.107	-0.610	0.713	-0.034	0.600	0.480	0.046
6-311 + + G( $2d,p$ )	0.690	0.750	0.102	-0.590	0.680	-0.030	0.579	0.450	0.043
6-311 + + G( $3d,p$ )	0.675	0.735	0.104	-0.576	0.667	-0.030	0.556	0.433	0.044
6-311 + + G( $2d,2p$ )	0.687	0.746	0.103	-0.587	0.676	-0.030	0.574	0.448	0.043
6-311 + + G( $3d,3p$ )	0.677	0.731	0.104	-0.577	0.661	-0.028	0.565	0.435	0.045
CISD level									
3-21G	0.442	0.564	0.108	-0.405	0.543	-0.048	0.143	0.106	0.042
6-31G( $d$ )	0.570	0.681	0.108	-0.489	0.624	-0.048	0.386	0.334	0.042
Experiment <sup>b</sup>	0.577	0.614	0.095	-0.481	0.539	-0.019	0.460	0.389	0.038

<sup>a</sup> In a.u. See Eqs. (4)–(6) for definitions of the invariants.

<sup>b</sup> See Ref. 10.

TABLE V. Calculated and experimental vibrational frequencies.<sup>a</sup>

Basis set	<i>A</i> <sub>1</sub>			<i>E</i>		
	<i>ν</i> <sub>1</sub>	<i>ν</i> <sub>2</sub>	<i>ν</i> <sub>3</sub>	<i>ν</i> <sub>4</sub>	<i>ν</i> <sub>5</sub>	<i>ν</i> <sub>6</sub>
HF level						
STO-3G	3556	1750	1372	3746	1784	1326
3-21G	3126	1685	1213	3184	1693	1320
4-31G	3113	1677	1188	3187	1681	1321
6-21G	3126	1690	1218	3184	1687	1322
D95	3154	1652	1197	3246	1661	1310
D95( <i>d</i> )	3185	1642	1123	3274	1646	1311
6-31G	3130	1675	1203	3209	1675	1318
6-31 + G	3133	1661	1187	3213	1667	1310
6-31 + + G	3132	1661	1185	3212	1665	1308
6-31G( <i>d</i> )	3161	1655	1124	3238	1659	1315
6-31G(2 <i>d</i> )	3117	1622	1088	3202	1640	1302
6-31G(3 <i>d</i> )	3147	1626	1107	3223	1642	1305
6-31G( <i>d,p</i> )	3140	1639	1125	3220	1638	1310
6-31G(2 <i>d,2p</i> )	3111	1622	1087	3190	1630	1302
6-31 + G( <i>d,p</i> )	3143	1629	1115	3224	1633	1305
6-31 + + G( <i>d,p</i> )	3143	1628	1114	3224	1632	1304
6-311G	3091	1665	1179	3167	1662	1315
6-311 + + G	3088	1650	1164	3166	1658	1309
6-311G( <i>d</i> )	3137	1645	1100	3214	1645	1316
6-311G( <i>d,p</i> )	3128	1628	1105	3205	1619	1302
6-311 + G( <i>d,p</i> )	3129	1617	1098	3207	1621	1297
6-311 + + G( <i>d,p</i> )	3129	1616	1098	3206	1620	1297
6-311 + + G(2 <i>d,p</i> )	3115	1616	1084	3190	1622	1300
6-311 + + G(3 <i>d,p</i> )	3122	1612	1082	3198	1621	1298
6-311 + + G(2 <i>d,2p</i> )	3110	1621	1085	3182	1627	1303
6-311 + + G(3 <i>d,2p</i> )	3103	1622	1082	3176	1626	1305
Correlated level						
CISD/3-21G	3109	1598	1213	3170	1601	1243
MP2/6-311G( <i>d,p</i> ) <sup>b</sup>	3088	1552	1107	3193	1526	1230
Est. 6-311 + + G(3 <i>d,3p</i> )	3063	1546	1084	3164	1533	1233
Exp. est. harmonic <sup>c</sup>	3031	1490	1059	3132	1498	1206
Exp. anharmonic <sup>c</sup>	2965	1460	1048	3006	1468	1182

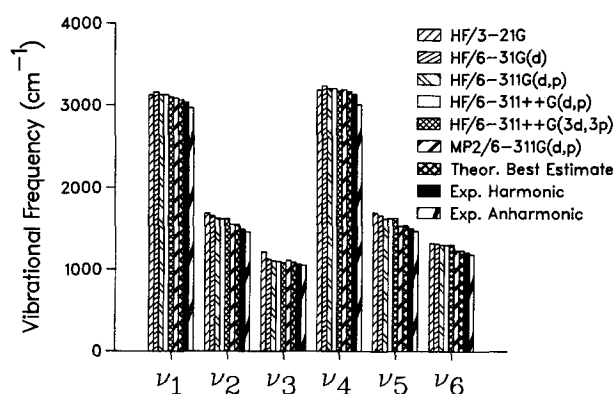
<sup>a</sup> In cm<sup>-1</sup><sup>b</sup> See Ref. 35; geometry  $R(\text{CH}) = 1.0917$ ,  $R(\text{CF}) = 1.3816$ ,  $\langle \text{HCF} \rangle = 109.20$  [almost identical to the CID/6-31G(*d*) geometry used for the present calculations].<sup>c</sup> See Ref. 29.

FIG. 4. Comparison of the calculated and experimental vibrational frequencies for selected basis sets.

polarized double split-valence basis [6-31G(*d*) or 6-31G(*d,p*)] to a triple split basis [6-31G(*d*) or 6-311G(*d,p*)] results in an additional 10–20 cm<sup>-1</sup> lowering. Compared with the experimental estimated harmonic frequencies, the Hartree–Fock frequencies calculated with the largest basis set, 6-311 + + G(3*d,3p*), are ~2% too high for the stretches and ~8% too high for the bends.

An estimate of the effect of correlation energy on the frequencies can be obtained from the CISD/3-21G and MP2/6-311G(*d,p*)<sup>35</sup> calculations. If compared with the Hartree–Fock calculations at the same geometry, the changes in frequency are quite similar: relatively small for bond stretching but more than 70 cm<sup>-1</sup> for the bending modes. The calculated frequencies obtained by adding the MP2/6-311G(*d,p*) correlation corrections<sup>35</sup> to the

HF/6-311 + + G(3*d*,3*p*) frequencies are only  $2.1 \pm 1.0\%$  higher than the experimental estimate of the harmonic frequencies.

### Infrared intensities

The calculated and experimental absolute infrared intensities are given in Table VI and Fig. 5. Because of overlapping bands, the sum of the intensities for  $\nu_1$  and  $\nu_4$  and for  $\nu_2$  and  $\nu_3$  can be measured more reliably than the individual intensities. These are also included in Table VI. The uncer-

tainties in the experimental intensities are estimated to be  $\pm 10\%$  for nonoverlapping bands and up to  $\pm 50\%$  for strongly overlapping bands.<sup>4</sup>

Unlike the frequencies, the calculated intensities show rather large basis set effects. A similar sensitivity to basis set effects has also been found for a variety of other small molecules.<sup>16</sup> The addition of *d* functions to the heavy atoms has the largest effect on  $A_3$  and  $A_4$ ; other intensities are changed by  $\pm 5$  km/mol. A second and a third set of *d* functions cause further changes in the intensities, primarily in  $A_3$  and

TABLE VI. Calculated and experimental infrared intensities.<sup>a</sup>

Basis set	$A_1$			$E$			$A_1 + A_4$	$A_2 + A_3$
	$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$		
HF level								
STO-3G	2.6	1.9	7.2	6.8	2.5	7.5	9.4	4.4
3-21G	19.3	7.7	70.6	108.0	2.9	2.8	127.3	10.6
4-31G	20.5	5.9	92.0	101.4	6.0	3.8	121.9	11.9
6-21G	20.3	8.1	69.5	115.8	2.4	2.8	136.1	10.5
D95	43.4	4.2	124.2	132.8	12.2	4.2	176.2	16.4
D95( <i>d</i> )	42.6	11.4	152.0	129.3	3.7	6.6	171.9	15.1
6-31G	22.2	6.9	97.3	99.1	6.8	3.8	121.3	13.4
6-31 + G	27.2	4.5	116.5	76.3	12.4	4.9	103.5	16.9
6-31 + + G	27.3	4.7	116.4	79.5	13.0	4.8	106.8	17.7
6-31G( <i>d</i> )	28.7	13.0	125.5	118.0	1.3	6.3	146.7	14.3
6-31G(2 <i>d</i> )	23.9	7.1	119.0	89.0	2.7	6.6	112.9	9.8
6-31G(3 <i>d</i> )	30.6	6.7	132.5	80.3	6.1	8.6	110.9	12.8
6-31G( <i>d</i> , <i>p</i> )	29.3	10.4	125.9	114.8	2.0	5.8	144.1	12.4
6-31G(2 <i>d</i> ,2 <i>p</i> )	28.8	4.9	118.1	101.9	3.0	5.1	130.7	7.9
6-31 + G( <i>d</i> , <i>p</i> )	36.9	7.5	152.0	91.0	5.8	6.6	127.9	13.3
6-31 + + G( <i>d</i> , <i>p</i> )	37.0	7.7	152.3	95.6	6.3	6.4	132.6	14.0
6-311G	27.7	7.9	108.5	108.2	9.0	6.0	135.9	16.9
6-311 + + G	31.1	5.6	119.6	93.6	12.6	5.6	127.7	18.2
6-311G( <i>d</i> )	32.2	9.6	141.8	127.7	4.6	7.2	159.9	14.2
6-311G( <i>d</i> , <i>p</i> )	29.2	7.8	139.1	109.3	5.7	6.5	138.5	13.5
6-311 + G( <i>d</i> , <i>p</i> )	34.8	6.2	156.4	92.7	8.7	6.5	127.5	14.9
6-311 + + G( <i>d</i> , <i>p</i> )	34.9	6.3	156.4	93.1	8.3	6.6	128.0	14.6
6-311 + + G(2 <i>d</i> , <i>p</i> )	32.8	3.9	148.2	91.8	8.2	6.9	124.6	12.1
6-311 + + G(3 <i>d</i> , <i>p</i> )	35.0	3.5	141.8	82.2	8.6	6.3	117.2	12.1
6-311 + + G(2 <i>d</i> ,2 <i>p</i> )	33.1	3.9	146.9	82.3	8.5	6.3	115.4	12.4
6-311 + + G(3 <i>d</i> ,3 <i>p</i> )	35.6	2.8	142.5	80.2	8.9	5.9	115.8	11.7
CISD level								
3-21G <sup>b</sup>	19.6	8.5	72.6	106.5	2.8	2.4	126.1	11.3
6-31G( <i>d</i> ) <sup>c</sup>	26.0	11.1	103.1	95.7	1.9	2.1	121.7	13.0
Est. 6-311 + + G(3 <i>d</i> ,3 <i>p</i> )	32.9	1.0	120.1	67.9	9.5	1.7	100.8	10.5
Experiment <sup>d</sup>	24.7	0.9	95.0	61.0	8.7	2.6	85.7	9.6
	$\pm 13$	$\pm 0.2$	$\pm 10$	$\pm 10$	$\pm 2$	$\pm 1$	$\pm 9$	$\pm 1$
Experiment <sup>e</sup>			95.5			2.8	84.9	9.8
Experiment <sup>f</sup>	37.4	3.4	108.3	37.4	6.0	1.7	74.8	9.4
Experiment <sup>g</sup>			116.0					
			$\pm 12$					

<sup>a</sup> In km/mol.

<sup>b</sup> Using the HF/3-21G normal coordinates.

<sup>c</sup> Using the HF/6-31G(2*d*) normal coordinates.

<sup>d</sup> See Ref. 4.

<sup>e</sup> See Ref. 3.

<sup>f</sup> See Ref. 2.

<sup>g</sup> See Ref. 5.

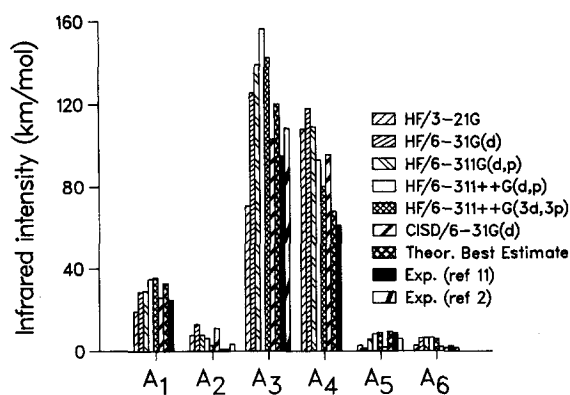


FIG. 5. Comparison of the calculated and experimental infrared intensities for selected basis sets.

$A_4$ . The effect of  $p$  functions is much smaller than  $d$  functions, except for  $A_4$ . Diffuse functions on the heavy atoms also influence  $A_3$  and  $A_4$  much more than the other intensities, but diffuse functions on hydrogen cause very little change. Similar to the dipole moment, the effects of multiple  $d$  functions and diffuse functions are not additive. Expansion of the basis set from 6-31G to 6-311G results in changes of  $-5$  to  $+20$  km/mol, both with and without polarization functions, but only changes of  $\pm 5$  km/mol if the diffuse functions are included. The agreement of the intensities calculated at the HF/6-311 + + G(3d,3p) level is quite good, with the exception of  $A_1$ ,  $A_3$ , and  $A_4$ .

Correlation corrections were estimated at the CISD/6-31G(2d) level. The largest changes are  $-22$  km/mol for  $A_3$  and  $A_4$ , with other intensities changing by less than 5 km/mol. If these changes are added to the HF/6-311 + + G(3d,3p) values, an estimate of the intensities at the CISD/6-311 + + G(3d,3p) level can be obtained. The correlation corrections significantly improve the agreement with experiment, although there is still room for improvement of  $A_1$ ,  $A_3$ , and  $A_4$ . The calculated value for  $A_3$ , 120.1 km/mol, agrees slightly better with the more recent measurement, 116 km/mol,<sup>5</sup> than with the earlier experimental values. However, some caution is required because of the size of the correlation correction. The experimental values for the sums  $A_1 + A_4$  and  $A_2 + A_5$  are in better agreement with each other than the individual intensities, because of difficulties in separating contributions from overlapping bands.<sup>4</sup> For the ratios of these intensities,  $A_1/A_4$  and  $A_2/A_5$ , there is very good agreement between the present calculations and the values quoted by Russell, Needham, and Overend.<sup>4</sup> Since  $\nu_1$  and  $\nu_4$  are CH stretching modes, better agreement for the individual intensities probably would require correlation corrections obtained from calculations that include polarization functions on hydrogen [e.g., CISD/6-31G( $d,p$ ) or better].

The calculated intensity for the  $\nu_3$  band can be analyzed further. Since  $\nu_3$  is almost pure C-F stretch,  $A_3$  is dominated by the dipole moment derivative (squared) of the C-F bond. The dipole moment derivative, with some assumptions, can be related to the C-F bond dipole. Because the C-F bond dipole is the main contributor to molecular dipole moment there should be a correlation between  $A_3$  and the square of

TABLE VII. Correlation between the intensity and the dipole moment for the CF stretching vibration.<sup>a</sup>

Level	$A_3$	$\mu$	$A_3/\mu^2$
HF/STO-3G	7.2	1.157	5.4
HF/3-21G	70.6	2.252	13.9
HF/4-31G	92.0	2.499	14.7
HF/6-21G	69.5	2.223	14.1
HF/6-31G	97.3	2.500	15.6
HF/D95	124.2	2.598	18.4
HF/6-311G	108.5	2.510	17.2
HF/6-31 + G	116.5	2.655	16.5
HF/6-31 + + G	116.4	2.655	16.5
HF/6-311 + + G	119.6	2.591	17.8
HF/D95( $d$ )	152.0	2.178	32.0
HF/6-31G( $d$ )	125.5	2.065	29.4
HF/6-31G(2d)	119.0	1.936	31.7
HF/6-31G(3d)	132.5	1.987	33.6
HF/6-31G( $d,p$ )	125.9	2.057	29.8
HF/6-31G(2d,2p)	118.1	1.939	31.4
HF/6-31 + G( $d,p$ )	152.0	2.235	30.4
HF/6-31 + + G( $d,p$ )	152.3	2.234	30.5
HF/6-311G( $d$ )	141.8	2.171	30.0
HF/6-311G( $d,p$ )	139.1	2.154	30.0
HF/6-311 + G( $d,p$ )	156.4	2.237	31.1
HF/6-311 + + G( $d,p$ )	156.4	2.238	31.2
HF/6-311 + + G(2d,p)	148.2	2.112	33.2
HF/6-311 + + G(3d,p)	141.8	2.060	33.4
HF/6-311 + + G(2d,2p)	146.9	2.113	32.9
HF/6-311 + + G(3d,3p)	142.5	2.063	33.5
CISD/3-21G	72.6	1.967	18.8
CISD/6-31G(2d)	103.1	1.794	32.0

<sup>a</sup> Intensities in km/mol, dipole moment in Debye.

the molecular dipole moment. This empirical relation is tested in Table VII. Once  $d$  functions are included in the basis set, the ratio  $A_3/\mu^2$  is remarkably constant,  $31.5 \pm 1.4$  for 17 entries. This suggests that  $A_3 = 142.5$  km/mol computed at the HF/6-311 + + G(3d,3p) level is very close to the Hartree-Fock limit, since the dipole moment at this level is very close to the estimated Hartree-Fock limit. Based on the ratio  $A_3/\mu^2 = 33.5$  [HF/6-311 + + G(3d,3p)] and the experimental dipole moment,  $\mu = 1.856$  D, a value of  $A_3 = 115 \pm 5$  km/mol can be predicted. More extensive calculations that include correlation corrections with much larger basis sets would be needed to make a more decisive selection among the experimental values.

## ACKNOWLEDGMENTS

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<sup>1</sup>(a) S. M. Freund, G. Duxbury, M. Romheld, J. T. Tiedje, and T. Oka, *J. Mol. Spectrosc.* **52**, 38 (1974); (b) E. Arimondo and T. Oka, *Phys. Rev. A* **26**, 1494 (1982).

<sup>2</sup>G. M. Barrow and D. C. McKean, *Proc. R. Soc. London Ser. A* **213**, 27 (1952).

<sup>3</sup>S. Kondo and S. Saeki, *J. Chem. Phys.* **76**, 809 (1982).

<sup>4</sup>J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.* **45**, 3383 (1966).

<sup>5</sup>A. G. Adam, T. E. Gough, N. R. Isenor, and G. Scoles, *Phys. Rev. A* **32**,



- 1451 (1985).
- <sup>6</sup>(a) J. F. Biarge, J. Herranz, and J. Morcillo, *An. R. Soc. Esp. Fis. Quim. A* **57**, 81 (1961); (b) J. Morcillo, M. Lastra, and J. F. Biarge, *ibid.* **57**, 81 (1961); (c) J. Morcillo, L. J. Zamorano, and J. M. V. Heredia, *Spectrochim. Acta* **22**, 1969 (1966); (d) J. Morcillo, J. F. Biarge, J. M. V. Heredia, and A. Medina, *J. Mol. Struct.* **3**, 77 (1969).
- <sup>7</sup>W. B. Person and D. Steele, *Mol. Spectrosc.* **2**, 357 (1974).
- <sup>8</sup>*Vibrational Intensities in Infrared and Raman Spectroscopy*, edited by W. B. Person and G. Zerbi (Elsevier, Amsterdam, 1982).
- <sup>9</sup>W. B. Person and J. H. Newton, *J. Chem. Phys.* **61**, 1040 (1974).
- <sup>10</sup>J. H. Newton and W. B. Person, *J. Chem. Phys.* **64**, 3036 (1976).
- <sup>11</sup>(a) W. B. Person, in *Vibrational Intensities in Infrared and Raman Spectroscopy*, edited by W. B. Person and G. Zerbi (Elsevier, Amsterdam, 1982), Chap. 14; (b) W. B. Person, B. Zilles, J. D. Rogers, and R. G. A. Maia, *J. Mol. Struct.* **80**, 297 (1980).
- <sup>12</sup>T. B. Lakdar, E. Taillandier, and G. Berthier, *Mol. Phys.* **39**, 881 (1980).
- <sup>13</sup>A. Komornicki and J. W. McIver, Jr., *J. Chem. Phys.* **70**, 2014 (1979).
- <sup>14</sup>J. Gerratt and I. M. Mills, *J. Chem. Phys.* **49**, 1719 (1968).
- <sup>15</sup>(a) R. D. Amos, *Chem. Phys. Lett.* **108**, 185 (1984); (b) R. D. Amos, in *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, edited by P. Jørgensen and J. Simons (Reidel, Dordrecht, 1985).
- <sup>16</sup>(a) Y. Yamaguchi, M. Frisch, J. Gaw, H. F. Schaefer, and J. S. Binkley, *J. Chem. Phys.* **84**, 2262 (1986); (b) M. J. Frisch, Y. Yamaguchi, J. F. Gaw, H. F. Schaefer, and J. S. Binkley, *ibid.* **84**, 531 (1986); (c) Extensive calculations on the IR and vibrational frequencies of water were presented by Y. Yamaguchi, at the 9th Canadian Symposium on Theoretical Chemistry, Toronto, Canada, June, 1986.
- <sup>17</sup>J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, *GAUSSIAN 82*, Carnegie-Mellon University, Pittsburgh, 1983.
- <sup>18</sup>D. J. DeFrees, K. Raghavachari, H. B. Schlegel, and J. A. Pople, *J. Am. Chem. Soc.* **104**, 5576 (1982).
- <sup>19</sup>R. A. Whiteside, M. J. Frisch, and J. A. Pople, *The Carnegie-Mellon Archive* (Carnegie-Mellon University, Pittsburgh, 1983).
- <sup>20</sup>J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem. Symp.* **13**, 225 (1979).
- <sup>21</sup>(a) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51**, 2567 (1969); (b) R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.* **54**, 724 (1971); (c) W. J. Hehre, R. Ditchfield, and J. A. Pople, *ibid.* **56**, 2257 (1972); (d) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta (Berlin)* **28**, 213 (1973); (e) M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984).
- <sup>22</sup>S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- <sup>23</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).
- <sup>24</sup>K. Raghavachari and J. A. Pople, *Int. J. Quantum Chem.* **20**, 1067 (1981).
- <sup>25</sup>W. T. King, G. B. Mast, and P. P. Blanchette, *J. Chem. Phys.* **56**, 4440 (1976).
- <sup>26</sup>W. T. King, in *Vibrational Intensities in Infrared and Raman Spectroscopy*, edited by W. B. Person and G. Zerbi (Elsevier, Amsterdam, 1982), Chap. 6.
- <sup>27</sup>W. B. Person, in *Vibrational Intensities in Infrared and Raman Spectroscopy*, edited by W. B. Person and G. Zerbi (Elsevier, Amsterdam, 1982), Chap. 4.
- <sup>28</sup>E. B. Wilson, J. C. Decius, and R. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
- <sup>29</sup>J. Duncan, D. C. McKean, and G. K. Spiers, *Mol. Phys.* **24**, 553 (1972).
- <sup>30</sup>C. E. Blom and A. Muller, *J. Mol. Spectrosc.* **70**, 449 (1978).
- <sup>31</sup>P. Pulay, J.-G. Lee, and J. E. Boggs, *J. Chem. Phys.* **79**, 3382 (1983).
- <sup>32</sup>R. Jaquet, W. Kutzelnigg, and V. Staemmler, *Theor. Chim. Acta (Berlin)* **54**, 205 (1980).
- <sup>33</sup>G. C. Lie, S. D. Peyerimhoff, and R. J. Buenker, *J. Chem. Phys.* **75**, 2892 (1981).
- <sup>34</sup>Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.* **73**, 2310 (1980).
- <sup>35</sup>(a) S. Kondo, Y. Koga, and T. Nakanaga, *J. Chem. Phys.* **81**, 1951 (1984); (b) S. Kondo, *ibid.* **81**, 5945 (1984).