An SCF–MO–CNDO Study of Equilibrium Geometries, Force Constants, and Bonding Energies: CNDO/BW.† Part III.[1] Triatomics and Polyatomics

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The CNDO/BW theory is applied to triatomic and polyatomic molecules and ions to calculate their spectroscopic ground states, equilibrium geometries, bonding energies, and force constants. The calculated results are compared to the experimental results and the results of other CNDO methods.

THE CNDO/BW method [1,2] is applied to triatomic and polyatomic molecules and ions. The calculated spectroscopic ground states, equilibrium geometries, bonding energies, and force constants, are compared to the experimental results and to the results predicted by other semiempirical and *ab initio* calculations.

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[1] Part II, R. J. Boyd and M. A. Whitehead, preceding paper.

[2] Part I, R. J. Boyd and M. A. Whitehead, *J.C.S. Dalton*, 1972, 73.

DISCUSSION

All parameter sets predict the spectroscopic ground states correctly for those triatomic molecules with known ground states. In a few cases for which there is no spectroscopic information, the method predicts two different states depending on the parameter set used.

The calculated equilibrium geometries (Table 1) agree well with experiment. All parameter sets predict correctly bent or linear equilibrium geometries where the equilibrium geometry is known. The mean deviations from experiment of the bond lengths not used to calibrate the molecular parameters are 0·025, 0·028, 0·031, and 0·035 Å for parameter sets (I)—(IV), and the corresponding deviations for the bond angles are 4·2, 3·2, 5·2, and 4·1°.

The bond angles are more sensitive to changes in the parameters and less accurate than the bond lengths. This is to be expected since the molecular parameters were chosen to yield bond lengths in agreement with experiment for a few molecules, but no attempt was made to calibrate the bond angles directly.[2] The inclusion of VSIP values in the evaluation of resonance integrals yields larger angles for nonlinear triatomic molecules than the simple overlap proportionality approximation, and leads to angles which are larger than observed, while the overlap approximation leads to angles which are too small. The simple overlap approximation leads to larger deviations for both bond lengths and angles.

The NO bonds in N_2O and N_2O^+, the CS bonds in COS, CS_2, and CS_2^+, and the SO bond in SO_2 are all predicted to be much longer than observed. The results for the series NO_2^+, NO_2, and NO_2^- agree very well with experiment but in NO^+, N_2O, and N_2O^+, the NO bond is consistently too long by 0·05 Å or more. There is no explanation of why some NO bonds are consistently well predicted and others are seriously overestimated, whereas for S the errors are in part due to the omission of 3*d* orbitals in the basis set.

Recent *ab initio* calculations [3-6] on SO, SO_2, O_2, and O_3 comparing the use of an *sp* versus *spd* basis set have shown that *d* orbitals are important in cases where S has ' an excess of valency '. When the S valency is 2 or less as in H_2S and SO, the *d* orbitals are unimportant; when the S valency is 4, as in SO_2, the *d* orbitals are important. The present results reflect this ' excess of valency ' idea, since we get good results for HS using parameters from H_2S, neither of which displays ' excess of valency,' but a much less successful result for SO_2 with parameters from SO, where SO_2 has ' excess of valency '; the S–O bond length is too long and the O–S–O angle too small: the CNDO/BW results are much better than the *ab initio* results using an *sp* basis and comparable with the *ab initio* results using an *spd* basis.

Both linear and bent ground states are predicted for CH_2^+, FH_2^+, FH_2, and ClH_2 depending on the parameters. Parameter set (I) predicts all four to be linear but BH_2 and H_2O, which are isoelectronic with CH_2^+

TABLE 1

Equilibrium geometries of triatomic and polyatomic molecules and ions [a]

Molecule [c]	(IVC) [d]	Parameter set [b]				
		(I)	(II)	(III)	(IV)	Expt.[e]
BH_2 (C_{2v})	R_{BH}	1·185		1·197		1·18
	θ_{HBH}	135·8		129·1		131
BH_2^+ (C_{2v})	R_{BH}	1·166		1·175		
	θ_{HBH}	180·0		180·0		
$^1CH_2$ (C_{2v})	R_{CH}	1·098	1·107	1·109	1·113	1·11
	θ_{HCH}	104·4	101·5	93·4	95·1	102·4
$^3CH_2$ (C_{2v})	R_{CH}	1·074	1·085	1·099	1·108	(1·071)[f]
	θ_{HCH}	148·4	135·8	131·7	131·5	(140)
CH_2^+ (C_{2v})	R_{CH}	1·090	1·084	1·113	1·105	
	θ_{HCH}	180·0	142·9	136·9	131·1	
NH_2 (C_{2v})	R_{NH}	1·013	1·009	1·021	1·011	1·024[g]
	θ_{HNH}	103·5	96·2	66·3	83·9	103·3
NH_2^+ (C_{2v})	R_{NH}	1·038	1·014	1·058	1·031	
	θ_{HNH}	119·2	99·1	58·3	67·0	
OH_2 (C_{2v})	θ_{HOH}	114·2	106·1	82·8	86·4	104·5
OH_2^+ (C_{2v})	R_{OH}	0·987	0·971	0·983	0·974	
	θ_{HOH}	161·1	126·2	98·1	86·2	
FH_2 (C_{2v})	R_{FH}	1·004	1·001	0·979	0·972	
	θ_{HFH}	180·0	180·0	180·0	144·3	
FH_2^+ (C_{2v})	R_{FH}	0·950	0·936	0·952	0·943	
	θ_{HFH}	180·0	180·0	118·8	102·1	
$^1SiH_2$ (C_{2v})	R_{SiH}	1·488	1·513	1·492	1·502	
	θ_{HSiH}	100·9	99·4	94·2	97·8	
$^3SiH_2$ (C_{2v})	R_{SiH}	1·470	1·514	1·490	1·524	
	θ_{HSiH}	135·7	133·5	128·3	137·6	
SiH_2^+ (C_{2v})	R_{SiH}	1·479	1·479	1·496	1·489	
	θ_{HSiH}	135·5	132·8	128·3	136·2	
PH_2 (C_{2v})	R_{PH}	1·414	1·415	1·416	1·419	1·428
	θ_{HPH}	101·4	95·5	93·0	92·6	91·5
PH_2^+ (C_{2v})	R_{PH}	1·432	1·399	1·433	1·398	
	θ_{HPH}	106·9	95·0	94·2	90·7	
SH_2 (C_{2v})	θ_{HSH}	103·0	96·2	91·8	89·0	92·2
SH_2^+ (C_{2v})	R_{SH}	1·348	1·333	1·347	1·332	
	θ_{HSH}	107·9	97·9	93·3	87·2	
ClH_2 (C_{2v})	R_{ClH}	1·376	1·366	1·359	1·342	
	θ_{HClH}	180·0	180·0	163·4	135·7	
ClH_2^+ (C_{2v})	R_{ClH}	1·303	1·292	1·303	1·292	
	θ_{HClH}	118·3	108·0	99·3	90·8	
HCN	R_{CH}	1·074	1·076	1·089	1·092	1·063
	θ_{HCN}	180·0	180·0	180·0	180·0	180·0
HCN^+	R_{CN}	1·144	1·213	1·223	1·227	
	R_{CH}	1·096	1·078	1·110	1·098	
	θ_{HCN}	180·0	180·0	180·0	180·0	
HNO	R_{NO}	1·186	1·178	1·187	1·174	1·212
	R_{NH}	1·024	1·020	1·010	1·016	1·063
	θ_{HNO}	106·4	106·8	98·3	104·5	108·6
BF_2 (C_{2v})	R_{BF}	1·293		1·293		
	θ_{FBF}	134·7		142·8		
CO_2 (C_{2v})	R_{CO}	1·167	1·171	1·182	1·186	1·160
	θ_{OCO}	180·0	180·0	180·0	180·0	180·0
CO_2^+ (C_{2v})	R_{CO}	1·172	1·176	1·185	1·189	1·177
	θ_{OCO}	180·0	180·0	180·0	180·0	180·0
CO_2^- (C_{2v})	R_{CO}	1·216	1·219	1·218	1·221	
	θ_{OCO}	145·7	145·0	147·5	146·6	
N_2O	R_{NN}	1·109	1·109	1·110	1·110	1·128
	R_{NO}	1·229	1·236	1·261	1·269	1·184
	θ_{NNO}	180·0	180·0	180·0	180·0	180·0
N_2O^+	R_{NN}	1·109	1·109	1·109	1·110	1·155
	R_{NO}	1·245	1·248	1·267	1·270	1·185
	θ_{NNO}	180·0	180·0	180·0	180·0	180·0
NO_2 (C_{2v})	R_{NO}	1·209	1·212	1·207	1·207	1·193
	θ_{ONO}	144·7	142·4	135·6	135·4	134·1
NO_2^+ (C_{2v})	R_{NO}	1·176	1·179	1·181	1·183	1·154
	θ_{ONO}	180·0	180·0	180·0	180·0	180·0
NO_2^- (C_{2v})	R_{NO}	1·250	1·251	1·244	1·241	1·236
	θ_{ONO}	130·3	129·6	123·7	124·0	115·4

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[3] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 158.

[4] I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1970, 1183.

[5] I. H. Hillier, ' Colloquia in Atomic and Molecular Structure ', Oxford, 1971.

[6] I. H. Hillier and V. R. Saunders, *Chem. Comm.*, 1970, 1510.

TABLE 1 (*Continued*)

Molecule[c]	Parameter set[b] (IVC)[d]	(I)	(II)	(III)	(IV)	Expt.[e]
O_3 (C_{2v})	R_{OO}	1·258	1·259	1·257	1·258	1·278
	θ_{OOO}	128·4	128·1	116·7	116·3	116·8
O_3^+ (C_{2v})	R_{OO}	1·226	1·227	1·236	1·237	
	θ_{OOO}	147·6	147·0	129·1	128·5	
COS	R_{CO}	1·155	1·153	1·165	1·162	1·160
	R_{CS}	1·594	1·600	1·622	1·636	1·560
	θ_{OCS}	180·0	180·0	180·0	180·0	180·0
COS^+	R_{CO}	1·134	1·135	1·138	1·139	
	R_{CS}	1·654	1·655	1·703	1·712	
	θ_{OCS}	180·0	180·0	180·0	180·0	
CS_2 (C_{2v})	R_{CS}	1·596	1·593	1·606	1·606	1·553
	θ_{SCS}	180·0	180·0	180·0	180·0	180·0
CS_2^+ (C_{2v})	R_{CS}	1·600	1·597	1·607	1·606	1·564
	θ_{SCS}	180·0	180·0	180·0	180·0	180·0
SO_2 (C_{2v})	R_{SO}	1·517	1·522	1·515	1·519	1·432
	θ_{OSO}	115·6	113·6	110·7	109·1	119·5
SO_2^+ (C_{2v})	R_{SO}	1·492	1·498	1·490	1·495	
	θ_{OSO}	120·4	117·2	116·1	113·8	
CH_3 (C_{3v})	R_{CH}	1·083	1·088	1·098	1·104	1·079
	θ_{HCH}	120·0	117·1	112·6	111·8	120·0
CH_3^+ (C_{3v})	R_{CH}	1·097	1·085	1·105	1·094	
	θ_{HCH}	120·0	120·0	120·0	120·0	
CH_3^- (C_{3v})	R_{CH}	1·124	1·148	1·134	1·151	
	θ_{HCH}	102·0	101·0	95·2	97·7	
NH_3 (C_{3v})	θ_{HNH}	102·9	95·9	80·3	87·1	106·6
NH_3^+ (C_{3v})	R_{NH}	1·029	1·003	1·025	1·019	
	θ_{HNH}	120·0	120·0	118·3	111·5	
NH_4^+ (T_d)	R_{NH}	1·026	1·005	1·015	1·011	(1·032)
OH_3 (C_{3v})	R_{OH}	1·012	1·004	0·980	0·977	
	θ_{HOH}	120·0	120·0	103·8	105·2	
OH_3^+ (C_{3v})	R_{OH}	0·977	0·963	0·976	0·973	(0·96)
	θ_{HOH}	120·0	120·0	92·8	87·8	(117)
PH_3 (C_{3v})	θ_{HPH}	101·6	95·5	93·0	93·1	93·3
PH_3^+ (C_{3v})	R_{PH}	1·422	1·401	1·431	1·422	
	θ_{HPH}	120·0	112·3	116·4	112·2	
PH_4^+ (T_d)	R_{PH}	1·423	1·394	1·425	1·417	1·42
BF_3 (C_{3v})	R_{BF}	1·310		1·306		1·295
	θ_{FBF}	120·0		120·0		120·0
CO_3^{2-} (C_{3v})	R_{CO}	1·292	1·297	1·302	1·309	1·29
	θ_{COO}	120·0	120·0	120·0	120·0	120·0
NO_3^- (C_{3v})	R_{NO}	1·291	1·295	1·289	1·292	1·268
	θ_{ONO}	120·0	120·0	120·0	120·0	120·0
CH_2O (C_{2v})	R_{CO}	1·171	1·161	1·186	1·180	1·203[h]
	R_{CH}	1·097	1·100	1·103	1·106	1·101
	θ_{HCH}	117·1	110·6	118·8	110·5	116·5
CH_2O^+ (C_{2v})	R_{CO}	1·173	1·176	1·186	1·188	
	R_{CH}	1·104	1·091	1·114	1·101	
	θ_{HCH}	131·3	126·1	148·8	135·8	
C_2H_2 ($D_{\infty h}$)	R_{CC}	1·258	1·269	1·237	1·244	1·203
	R_{CH}	1·070	1·068	1·080	1·078	1·061
$C_2H_2^+$ ($D_{\infty h}$)	R_{CC}	1·320	1·333	1·310	1·321	
	R_{CH}	1·084	1·074	1·101	1·092	
C_2H_4 (D_{2h})	R_{CC}	1·376	1·383	1·364	1·368	1·337
	R_{CH}	1·092	1·093	1·095	1·096	1·086
	θ_{HCH}	114·9	112·6	118·8	116·2	117·3
$C_2H_4^+$ (D_{2h})	R_{CC}	1·323	1·473	1·308	1·477	
	R_{CH}	1·107	1·089	1·113	1·096	
	θ_{HCH}	92·5	116·0	103·2	120·7	
C_2H_6 (D_3)	R_{CH}	1·099	1·101	1·099	1·100	1·093
	θ_{HCH}	107·7	106·8	109·4	108·2	107·8
	ω[i]	180·0	180·0	180·0	180·0	180·0

[a] Bond lengths in Å, angles in deg. [b] Parameter sets are: (I) resonance integrals from equation (12) with Hinze and Jaffé atomic parameters; (II) equation (12) with Hartree–Fock atomic parameters; (III) resonance integrals from equation (11) with Hinze and Jaffé parameters; (IV) equation (11) with Hartree–Fock atomic parameters, all from ref. 2. [c] Symmetry constraints are given in parentheses. [d] Bond lengths used for calibration of bonding and core repulsion parameters were: OH, SH, CN, BH, CH, NH, SiH, PH, and CC; bonds in OH_2, SH_2, HCN, BH_3, CH_4, NH_3, SiH_4, PH_3, and C_2H_6 respectively. [e] From refs. 7 and 24 except where noted otherwise. [f] G. Herzberg, *Proc. Roy. Soc.*, 1961, *A*, **262**, 291. [g] K. Dressler and D. A. Ramsey, *Phil. Trans.*, 1959, *A*, **251**, 553. [h] K. Tagaki and T. Oka, *J. Phys. Soc.* (*Japan*), 1963, **18**, 1174. [i] Dihedral angle.

and FH_2^+ respectively, have bent ground states[7] and, therefore, in the absence of structural data, the predictions that CH_2^+ and FH_2^+ are bent by parameter sets (II), (III), and (IV) for CH_2^+ and parameter sets (III) and (IV) for FH_2^+ seem more reasonable.[8]

The valence-shell electron configurations for FH_2 and ClH_2 are $2\sigma_g^2 1\sigma_u^2 1\pi_u^4 3\sigma_g$ and $3\sigma_g^2 2\sigma_u^2 2\pi_u^4 4\sigma_g$, respectively, in the linear form and $2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1$ and $4a_1^2 2b_2^2 5a_1^2 2b_1^2 6a_1$, respectively, in the bent form. The $1b_2$ and $3a_1$ orbitals in FH_2 and the $2b_2$ and $5a_1$ orbitals in ClH_2 may be interchanged depending on the parameters. The singly occupied σ_g orbital is formed from the valence-shell *s* orbitals and is antibonding between the halogen and hydrogen atoms. The singly occupied a_1 orbital is formed from the valence-shell *p* orbital lying along the C_2 axis of the molecule and the valence-shell *s* orbitals. The a_1 orbital is antibonding between the halogen atom and the hydrogens.

From the form of the a_1 orbital it is apparent that increasing the H–X–H angle lowers the energy of the a_1 orbital. Thus if FH_2 and ClH_2 are thought of as being formed from FH_2^+ and ClH_2^+ molecules with bent structures like H_2O, the addition of the ninth valence-shell electron to the a_1 orbital should lead to an increase in the H–X–H angle. Therefore, FH_2 and ClH_2 are expected to have larger bond angles than their unipositive ions.

The lowest singlet of CH_2 has been shown spectroscopically to be bent, but the geometry of the lowest triplet is uncertain,[7] although it is generally assumed to be linear. The present CNDO/BW method predicts a bent triplet in agreement with recent *ab initio* calculations[9] (135·1° and 1·096 Å), which predict a relatively flat potential surface, between 135 and 180°, with the most stable calculated linear geometry of 1·083 Å, only 6·7 kcal mole^{-1} greater than the calculated equilibrium geometry.

The NH_2 molecule is predicted to have a bent $^2B_1$ ground state in agreement with experiment, however parameter sets (III) and (IV) predict a very small H–N–H angle, owing to orbital rearrangement. Parameter sets (I) and (II) yield $2a_1^2 1b_2^2 3a_1^2 1b_1$ whereas parameter sets (III) and (IV) predict that $3a_1$ lies below $1b_2$. The $3a_1$ orbital is bonding between the $2p$ orbital on N, which lies along the C_2 axis of the NH_2 molecule, and the hydrogen $1s$ orbitals and is antibonding between the nitrogen $2s$ orbital and the hydrogen $1s$ orbital. The $1b_2$ orbital is bonding between the hydrogen $1s$ orbitals and the nitrogen $2p$ orbital perpendicular to the C_2 axis and in the plane of the molecule. Unlike the $3a_1$ orbital, the $1b_2$ is antibonding between the hydrogen $1s$ orbitals. Thus the $3a_1$ orbital energy is lowered with decreasing angle, while the $1b_2$ orbital favours the linear

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[7] G. Herzberg, ' Electronic Spectra and Electronic Structure of Polyatomic Molecules,' Van Nostrand, Princeton, New Jersey, 1966.

[8] A. D. Walsh, *J. Chem. Soc.*, 1953, 2260.

[9] C. F. Bender and H. F. Schaeffer, *J. Amer. Chem. Soc.*, 1970, **92**, 4984.

TABLE 2

Bonding energies [a] of triatomic and polyatomic molecules and ions and their dissociation products

Molecule [c]	Parameter set [b]				Expt. [d]
	(I)	(II)	(III)	(IV)	
BH_2	7·433		7·482		7·7
BH_2^+ (B^+)	7·219		6·841		
$^1CH_2$	9·165	9·275	9·783	10·212	9·41
$^3CH_2$	8·317	8·005	7·995	7·947	
CH_2^+ (C^+)	8·918	8·080	8·452	7·906	
NH_2	8·646	8·658	8·513	8·509	8·10
NH_2^+ (H^+)	9·897	9·169 (N^+)	9·468	8·801 (N^+)	
OH_2	10·063	10·058	10·060	10·060	10·06
OH_2^+ (H^+)	10·939	11·847	10·230	10·208	
FH_2	6·786	7·240	7·547	7·991	
FH_2^+ (H^+)	12·185	13·290	11·406	12·335	
$^1SiH_2$	7·030	7·372	7·534	8·347	
$^3SiH_2$	6·023	5·544	5·898	5·797	
SiH_2^+ (Si^+)	6·023	5·513	5·902	5·756	
PH_2	6·977	6·964	6·972	6·930	6·9
PH_2^+ (P^+)	7·563	6·807	7·410	6·727	
SH_2	7·882	7·879	7·881	7·881	7·881
SH_2^+ (S^+)	8·458	8·034	8·335	7·915	
ClH_2	5·201	5·549	5·509	5·858	
ClH_2^+ (H^+)	10·317	10·123 (Cl^+)	10·125	9·919 (Cl^+)	
HCN	13·539	13·537	13·537	13·537	13·537
HCN^+ (C^+)	11·301	11·505	11·218	11·045	
HNO	9·818	9·931	9·680	9·886	9·0
BF_2	12·381		11·960		13·1
CO_2	17·720	17·424	16·408	16·076	16·856
CO_2^+ (C^+)	15·091	15·142	13·423	13·382	
CO_2^- (O^-)	16·414	16·292	15·984	15·898	15·8
N_2O	12·723	12·593	12·030	11·941	11·724
N_2O^+ (N^+)	13·739	13·571	12·777	12·643	
NO_2	9·333	9·221	9·506	9·539	9·85
NO_2^+ (N^+)	10·483	10·217	10·316	10·187	
NO_2^- (N^-)	10·552	10·520 (O^-)	10·921	11·002 (O^-)	
O_3	6·684	6·592	7·434	7·434	6·35
O_3^+	8·993	8·931	9·239	9·230	
COS	15·661	15·609	14·207	14·067	14·42
COS^+ (C^+)	14·946	14·750	13·464	13·167	
CS_2	12·751	12·849	11·549	11·535	11·98
CS_2^+ (C^+)	12·986	12·657	11·678	11·243	
SO_2	8·642	8·196	9·324	8·935	11·177
SO_2^+ (S^+)	8·563	8·531	9·169	9·212	
BH_3	12·104		12·100		12·1
CH_3	13·419	13·185	13·230	13·415	13·4
CH_3^+ (C^+)	14·048	13·133	13·664	12·733	
CH_3^- (H^-)	13·963	13·309	15·140	14·898	
CH_4	18·179	18·175	18·180	18·180	18·180
NH_3	12·922	12·934	12·930	12·930	12·93
NH_3^+ (H^+)	14·862	13·251 (N^+)	13·119	11·316 (N^+)	
NH_4^+ (H^+)	19·767	17·867 (N^+)	17·793	15·035 (N^+)	
OH_3	10·988	11·544	12·056	12·498	
OH_3^+ (H^+)	17·068	17·674	16·185	16·904	16·8
SiH_4	13·866	13·871	13·871	13·870	13·87
PH_3	10·465	10·467	10·470	10·470	10·47
PH_3^+ (P^+)	11·129	8·891	10·138	7·992	
PH_4^+ (P^+)	15·007	12·391	13·983	10·327	
BF_3	19·349		18·015		20·1
CO_3^{2-} (O^-)	18·408	15·938	17·182	14·699	
NO_3^- (N^-)	13·440	13·272 (O^-)	13·821	13·811 (O^-)	
CH_2O	17·629	17·639	16·567	16·460	16·3
CH_2O^+ (C^+)	17·197	16·484	16·149	15·221	
C_2H_2	15·795	15·113	15·301	14·455	17·53
$C_2H_2^+$ (C^+)	15·562	14·422	14·677	13·325	
C_2H_4	23·245	22·940	22·875	22·469	24·36
$C_2H_4^+$ (C^+)	22·839	22·375	22·313	21·606	
C_2H_6	30·818	30·817	30·817	30·818	30·818

[a] In eV. [b] Parameter sets are defined in Table 1. [c] Dissociation products are in parentheses. [d] Calc. from data in refs. 25 and 26

form. With parameter sets (III) and (IV), the reverse pertains. This effect is also observed for NH_2^+.

The bonding energies of the triatomic molecules compare well with experiment, and the results (Table 2) are comparable to those from CNDO/SW.[10-12] The experimental trends for AH_2 molecules, and for series such as CO_2, COS, and CS_2 are reproduced correctly by the present method. For the latter molecules and non-hydride triatomic molecules, the bonding energy is overestimated by parameter sets (I) and (II), and underestimated by parameter sets (III) and (IV). The

TABLE 3

Force constants of polyatomic molecules [a]

Molecule	Type	Parameter set [b]				Expt.
		(I)	(II)	(III)	(IV)	
BH_2	BH	3·9		3·7		
	HBH	0·36		0·46		
BH_2^+	BH	4·2		4·0		
	HBH	0·35		0·36		
$^1CH_2$	CH	5·8	5·6	5·6	5·4	4·8 [c]
	HCH	0·55	0·68	0·67	0·80	0·58
$^3CH_2$	CH	6·3	5·6	5·4	5·0	
	HCH	0·28	0·57	0·66	0·66	
CH_2^+	CH	5·9	5·9	5·2	5·2	
	HCH	0·02	0·39	0·49	0·68	
NH_2	NH	7·3	7·2	6·5	6·6	
	HNH	0·38	0·67	0·46	0·60	
NH_2^+	NH	6·3	7·0	5·4	6·2	
	HNH	0·22	0·43	0·91	0·41	
OH_2	OH	10·0	10·0	9·1	9·2	8·4 [d]
	HOH	0·45	0·66	0·58	0·90	0·76
OH_2^+	OH	8·3	9·2	7·5	8·2	
	HOH	0·03	0·31	0·30	0·46	
FH_2	FH	7·2	8·0	7·4	8·2	
	HFH	0·15	0·19	0·03	0·18	
FH_2^+	FH	10·0	11·6	9·0	10·2	
	HFH	0·13	0·04	0·31	0·57	
$^1SiH_2$	SiH	2·8	2·5	2·8	2·6	
	HSiH	0·31	0·38	0·35	0·41	
$^3SiH_2$	SiH	2·9	2·2	2·6	2·1	
	HSiH	0·23	0·23	0·32	0·18	
SiH_2^+	SiH	2·7	2·5	2·5	2·4	
	HSiH	0·23	0·25	0·31	0·21	
PH_2	PH	3·7	3·3	3·6	3·2	
	HPH	0·37	0·42	0·38	0·40	
PH_2^+	PH	3·5	3·5	3·3	3·4	
	HPH	0·27	0·40	0·28	0·38	
SH_2	SH	4·6	4·5	4·4	4·3	4·3 [d]
	HSH	0·37	0·48	0·38	0·45	0·44
SH_2^+	SH	4·3	4·4	4·1	4·2	
	HSH	0·29	0·40	0·29	0·35	
ClH_2	ClH	3·6	3·7	3·6	3·9	
	HClH	0·08	0·01	0·03	0·22	
ClH_2^+	ClH	5·1	5·4	4·9	5·1	
	HClH	0·25	0·38	0·32	0·40	
HCN	CN	18·6	19·4	17·5	17·6	18·8 [e]
	CH	6·4	6·2	6·0	5·7	6·2
	HCN	0·30	0·31	0·25	0·26	0·21
HCN^+	CN	18·5	14·5	13·3	13·3	
	CH	5·3	6·0	5·2	5·4	
	HCN	0·07	0·07	0·03	0·03	
HNO	NO	17·6	17·6	16·0	16·6	10·5 [f]
	NH	6·8	6·7	6·5	6·1	7·2
	HNO	0·69	0·96	0·66	0·90	0·55
BF_2	BF	9·8		8·4		4·5 [g]
	FBF	0·63		0·19		0·58

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TABLE 3 (*Continued*)

Molecule	Type	Parameter set [b] (I)	(II)	(III)	(IV)	Expt.
CO_2	CO	19·2	19·2	15·8	15·6	17·3 [h]
	OCO	0·70	0·67	0·47	0·44	0·58
CO_2^+	CO	18·4	18·4	15·5	15·1	
	OCO	0·49	0·47	0·29	0·27	
CO_2^-	CO	15·7	15·7	13·3	13·2	
	OCO	1·08	1·07	0·57	0·54	
N_2O	NN	20·5	21·2	19·1	19·5	17·9 [i]
	NO	9·6	9·1	6·8	6·5	11·4
	NNO	0·33	0·30	0·20	0·18	0·49
N_2O^+	NN	19·8	23·2	17·7	17·7	
	NO	9·7	9·5	7·7	7·6	
	NNO	0·20	0·18	0·08	0·06	
NO_2	NO	15·8	15·1	14·0	15·5	13·0 [j]
	ONO	0·70	0·90	0·83	1·91	1·12
NO_2^+	NO	18·4	18·0	15·4	15·2	17·3 [i]
	ONO	0·39	0·35	0·24	0·22	0·42
NO_2^-	NO	13·3	13·3	12·3	15·5	7·7 [k]
	ONO	1·24	1·34	1·17	1·18	1·75
O_3	OO	19·1	18·0	16·8	16·4	5·7 [l]
	OOO	1·22	1·28	1·34	1·38	1·28
O_3^+	OO	20·7	20·7	17·2	17·0	
	OOO	0·51	0·54	0·98	1·04	
COS	CO	18·4	18·8	15·1	15·5	14·2 [c]
	CS	7·9	7·5	5·6	6·0	8·0
	OCS	0·49	0·47	0·32	0·30	0·37
COS^+	CO	20·1	20·2	17·9	17·9	
	CS	5·5	5·3	4·0	3·8	
	OCS	0·33	0·32	0·21	0·20	
CS_2	CS	9·6	9·4	7·9	7·6	7·9 [m]
	SCS	0·45	0·44	0·31	0·29	0·24
CS_2^+	CS	9·2	8·9	7·7	7·4	
	SCS	0·33	0·31	0·17	0·15	
SO_2	SO	10·9	11·3	9·6	9·3	10·0 [n]
	OSO	0·92	0·98	0·75	0·76	0·79
SO_2^+	SO	11·5	10·0	10·1	9·9	
	OSO	0·74	0·87	0·61	0·67	
BH_3	BH	4·1		4·1		
	HBH	0·42		0·44		
CH_3	CH	6·3	6·1	5·6	5·4	
	HCH	0·13	0·32	0·61	0·73	
CH_3^+	CH	5·9	6·1	5·5	5·7	
	HCH	0·63	0·65	0·70	0·72	
CH_3^-	CH	5·0	4·4	4·8	4·5	
	HCH	0·55	0·69	0·74	0·77	
CH_4	CH	6·1	6·1	6·0	5·9	5·8 [o]
NH_3	NH	7·4	7·2	6·9	6·7	7·1 [o]
	HNH	0·32	0·66	0·59	0·74	0·53
NH_3^+	NH	6·8	7·3	5·9	6·0	
	HNH	0·37	0·15	0·13	0·75	
NH_4^+	NH	7·1	7·5	6·4	6·5	
OH_3	OH	7·5	7·9	7·8	8·1	
	HOH	0·14	0·15	0·25	0·51	
OH_3^+	OH	9·2	9·9	8·2	8·6	
	HOH	0·16	0·01	0·45	0·73	
SiH_4	SiH	2·9	2·9	2·9	2·8	2·8 [o]
PH_3	PH	3·8	3·3	3·6	3·2	3·4 [o]
	HPH	0·29	0·41	0·37	0·40	0·34
PH_3^+	PH	3·6	3·3	3·3	2·9	
	HPH	0·12	0·38	0·15	0·42	
PH_4^+	PH	3·7	3·5	3·4	3·1	
BF_3	BF	11·0		9·2		6·4
	FBF	0·68		0·44		0·52
CO_3^{2-}	CO	13·2	13·0	10·8	10·5	
	OCO	1·42	1·37	0·99	0·91	
NO_3^-	NO	11·5	11·3	10·3	10·3	10·4 [i]
	ONO	0·90	0·88	0·59	0·57	1·45
CH_2O	CO	17·9	18·4	15·2	14·9	13·0 [p]
	CH	5·9	5·7	5·6	5·4	5·2
	HCH	0·65	0·75	0·62	0·76	0·80
CH_2O^+	CO	15·2	15·2	13·3	13·0	
	CH	5·5	5·7	5·5	5·3	
	HCH	0·36	0·44	0·13	0·22	
C_2H_2	CC	15·0	15·4	15·4	15·5	16·3 [d]
	CH	6·4	6·6	6·1	6·1	6·3
$C_2H_2^+$	CC	12·4	12·5	12·5	12·1	
	CH	6·1	6·3	5·4	5·6	
C_2H_4	CC	10·0	10·4	10·0	10·0	10·9 [q]
	CH	6·2	5·9	5·8	5·6	6·2
	HCH	0·64	0·72	0·65	0·72	0·65
$C_2H_4^+$	CC	12·0	7·6	12·1	7·2	
	CH	5·5	6·0	5·1	5·6	
	HCH	0·26	0·65	0·30	0·67	
C_2H_6	CC	5·9	6·0	5·8	5·7	4·6 [r]
	CH	5·9	5·8	5·8	5·7	5·3
	HCH	0·57	0·67	0·56	0·67	1·24

[a] All force constants in mdyn Å^{-1}; the bending force constant for an angle A–B–C is scaled by the inverse product of the A–B and B–C bond lengths. [b] Parameter sets are defined in Table 1. [c] G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules', Van Nostrand, Princeton, 1945. [d] J. W. Nibler and G. C. Pimentel, *J. Mol. Spectroscopy*, 1968, **26**, 294. [e] I. Suzuki, M. A. Pariseau, and J. Overend, *J. Chem. Phys.*, 1966, **44**, 3561. [f] K. B. Harvey and H. W. Brown, *J. chim. Phys.*, 1959, **56**, 745. [g] G. Nagarajan, *Austral. J. Chem.*, 1963, **16**, 717. [h] M. A. Pariseau, I. Suzuki, and J. Overend, *J. Chem. Phys.*, 1965, **42**, 2335. [i] R. Teranishi and J. C. Desius, *J. Chem. Phys.*, 1954, **22**, 896. [j] D. C. McKean, *Spectrochim. Acta*, 1966, **22**, 269. [k] R. E. Weston and T. F. Brodasky, *J. Chem. Phys.*, 1957, **27**, 683. [l] L. Pierce, *J. Chem. Phys.*, 1956, **24**, 139. [m] K. Kuchitsu and Y. Morino, *Bull. Chem. Soc. Japan*, 1965, **38**, 805. [n] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, 1954, **22**, 900. [o] J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, 1964, **20**, 523. [p] E. C. Curtis, *J. Mol. Spectroscopy*, 1964, **14**, 279, 292. [q] B. L. Crawford, J. E. Lancaster, and R. G. Inskeep, *J. Chem. Phys.*, 1953, **21**, 678. [r] J. Aldous and I. M. Mills, *Spectrochim. Acta*, 1963, **19**, 1567.

bonding energy of SO_2 is underestimated owing to lack of *d* orbitals in the basis set[13] as in CNDO/SW,[10-12] although greater separation for the bonding energies of O_3 and SO_2 has been obtained.

Unfortunately there is a lack of experimental data for the bonding energies of the ions in Table 2. Both sets of atomic parameters predict CO_2^- dissociates to give the experimentally observed O^-.[14] The parameters derived from Hinze and Jaffé valence states predict NO_2^- to give N^-, but the Hartree–Fock valence states predict the observed O^-.[14]

Force constants for symmetric stretching and bonding modes of triatomic molecules compare well with experiment (Table 3). There are insufficient experimental data to make an empirical choice between the four parameter sets. The simple overlap proportionality[1] for the resonance integrals yields lower force constants than the proportionality dependent on VSIP values.

The results for CO_2 and HCN compare very favourably with recent *ab initio* calculations[15] which give 19·5, 8·0, and 26·9 mdyn Å^{-1} for the CO, CH, and CN stretching force constants respectively and 0·41 and 0·36 mdyn Å^{-1} for the OCO and HCN bending force constants respectively. *Ab initio* studies of the potential surfaces of the other triatomic molecules have not been reported.

The OO stretching force constant of O_3 is too large, as in the case of O_2, whereas the force constant of NO is

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too large but in N_2O it is underestimated, and the calculated equilibrium bond lengths are too short and too long for the N–N and N–O bonds respectively. In contrast, the calculated NO equilibrium bond length in HNO is less than the observed value, and the calculated force constant is overestimated.

The calculated ground states of the polyatomic molecules agree with experiment. For the CH_3 radical, two different ground states are predicted depending on the parameters; the ground state of CH_3 is planar, $^2A_2''$, although it may be slightly nonplanar.[7,16,17] The parameter sets (I) and (II) calculations are, therefore, the more satisfactory. Inclusion of VSIP values in the resonance integrals leads to similar effects for other AH_3 molecules for which there are no experimental data.

Agreement between the calculated and observed equilibrium geometries of polyatomic molecules (Table 1) is good. The mean deviations from experiment of the bond lengths not used to calibrate are 0·016, 0·021, 0·015, and 0·019 Å for parameter sets (I)—(IV); the corresponding deviations for bond angles are 1·5, 2·7, 3·9, and 3·5°.

The observed trend for single, double, and triple CC bonds of hydrocarbons is reproduced, with lengthening of the C_2H_2 and C_2H_4 bonds. In contrast recent *ab initio* calculations account for the C_2H_6 bond but shorten the C_2H_2 and C_2H_4 bonds by 0·035 and 0·025 Å respectively.[15] The CNDO/2 method predicts bonds which are short by 0·006, 0·026, and 0·075 Å for C_2H_2, C_2H_4, and C_2H_6 respectively,[18] which cannot be fitted by adjusting the CNDO/2 carbon bonding parameter.[19] The Fischer–Kollmar modification [18] yields deviations of 0·010, 0·005, and −0·014 Å for C_2H_2, C_2H_4, and C_2H_6 (where the negative sign indicates the calculated bond is too short) by optimizing all empirical parameters for a large number of hydrocarbon molecules. By a similar procedure, Dewar and Haselbach [20] optimized their MINDO/2 method to give deviations of −0·003, −0·002, and −0·010 Å for C_2H_2, C_2H_4, and C_2H_6 respectively.

The bonding energies of the polyatomic molecules in Table 2 are in reasonable agreement with experimental data where this is available. The bonding energies of C_2H_2 and C_2H_4 are too low with all parameter sets, and the CO bond in formaldehyde is underestimated and consequently the bonding energy is greater than the observed value.

The force constants of the polyatomic molecules reproduce most observed trends and are as reliable as those of the triatomic molecules (Table 3). The deviations from experiment parallel those for the calculated equilibrium geometries and bonding energies. The force constants of the CC bond of the series C_2H_2, C_2H_4, and C_2H_6 are qualitatively very good, although those for C_2H_2 and C_2H_4 are low relative to that of C_2H_6, and are less accurate than by a recent theory, specifically designed for C_2H_4 alone.[21]

The simple overlap approximation for the resonance integrals leads to lower stretching force constants. Hinze and Jaffé valence-state data predict that the CC stretching force constant of $C_2H_4^+$ is larger than that of C_2H_4 and that ionization of C_2H_4 leads to a shorter CC bond length: opposite effects are predicted by Hartree–Fock atomic parameters. These differences are due to an orbital rearrangement of $C_2H_4^+$.

General Discussion.—The mean deviations from experiment of the bond lengths of all molecules not used in the calibration are 0·022, 0·025, 0·024, and 0·028 Å for parameter sets (I)—(IV). The deviations for the bond angles are 3·4, 3·1, 4·8, and 4·1° comparing favourably with *ab initio* calculations which have an average deviation of calculated and experimental bond lengths and angles of 0·035 Å and 1·7°.[15] For those molecules not used in parameterization the present results are better than those of a recent theory for the interhalogens.[22] The semiempirical results are not restricted to first-row atoms only; thus the mean deviations obtained include the relatively poor results obtained for CS and SO bonds.

The method differentiates between bent and linear structures and between planar and nonplanar structures. The mean deviations for the angles are largely due to a few molecules, the angles of which are very sensitive to changes in the parameters. The inclusion of VSIP values in the evaluation of resonance integrals generally predicts larger angles than the simple overlap proportionality.

The equilibrium geometries of many of the molecules were subject to certain symmetry constraints. Several calculations were repeated with the symmetry constraints removed. In every case the calculated equilibrium geometry was the same as with constraints.

The CNDO/BW [2] calculation of molecular potential surfaces yields good bonding energies comparable to the CNDO/SW results, based on experimental equilibrium geometry,[10-12] and yields better bonding energies than the Hartree–Fock method or other semiempirical methods, such as CNDO/2 [23] or extended Huckel theory.[11]

No particular parameter set yields consistently better bonding energies, and the average absolute deviations are not appreciably affected by changes in the parameters, although the bonding energies of individual molecules are sensitive. Slightly better bonding energies are obtained with atomic parameters evaluated from Hinze and Jaffé valence states. While the simple overlap pro-

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portionality for the resonance integrals yields slightly lower average deviations than the approximation in which VSIP values are included in the evaluation of resonance integrals. All parameters have been applied to both closed and open-shell configurations, and the parameterization is equally successful for closed and open-shell configurations.

Conclusion.—The CNDO/BW theory in no way alters the results or conclusions previously derived for dipole moments and quadrupole coupling constants by the CNDO/SW method.[27,28]

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