tetrahedron complexes, we believe that this approach is a useful one because:

(*a*) It permits, based on the generalized $(8-N)$ rule, a systematization of the structures.

(*b*) It allows the recognition of certain systematic trends such as the equipartition of the $C'—A—C'$ links, the competition of $C'—C'$ bonds with lone pairs, and so on.

(*c*) It will aide the synthesis of new compounds with particular structural features.

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Electron Density Distribution around Hydrogen Atoms in Linear Molecules

By S. Ikuta

General Education Department, Tokyo Metropolitan University, Yakumo, Meguro-ku, Tokyo 152, *Japan*

and M. Ishikawa, M. Katada and H. Sano

Faculty of Science, Tokyo Metropolitan University, Fukasawa, Setagayaku, Tokyo 158, *Japan*

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Abstract

Electron densities around H atoms in linear HX molecules (X = H, F, Cl, OLi, ONa, CN, CP, BeH, Li and Na) were calculated in two directions relating to the major and minor radii. A Hartree–Fock level of theory with the 6-311G(2*d*,*p*) or MC-311G(2*d*,*p*) basis sets was applied. Van der Waals radii of the H atoms in the isolated molecules were estimated at the position where the electron density is 0·005 a.u. (0·0337 e Å^{-3}). The anisotropy of both the electron density distributions and the van der Waals radii of the H atoms was clearly confirmed in all the molecules. The radii and the degree of anisotropy are linearly related to both the Mulliken atomic charges on the H atom and the electronegativity of the substituent X. The minor radius of the H atom depends strongly on the substituent X and increases as the electronegativity of X decreases. The predicted radii provide us with useful hints for considering the size of the H atom in molecules in the crystal.

1. Introduction

The van der Waals radius of an atom in molecules in the major direction (sideways-on radius, r_s), which is perpendicular to the chemical bond, is usually larger than that in the minor direction (head-on radius, r_h) parallel to the chemical bond. This is called 'polar flattening' and has been pointed out quantitatively by Nyburg & Faerman (1985). They examined many

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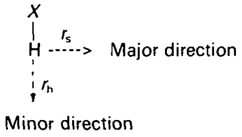
crystallographical data of non-bonded atoms bonded to a C atom.



Bader, Hennecker & Cade (1967) pointed out that the atoms and bonds in molecules are uniquely defined by the topology of the molecular electron density distribution, and recently proposed the volume of an atom in a molecule (Bader, Carrol, Cheeseman & Chang, 1987). However, there are few reports which quantitatively discuss the anisotropy of van der Waals radii ($r_s - r_h$) and electron density distribution around atoms in isolated molecules.

Recently, one of the present authors has theoretically confirmed the polar flattening of several atoms (F, Cl, Br, O and S atoms) in isolated molecules (Ikuta, 1989*a*,*b*). A small *negative* polar flattening was first reported on the P atom in an isolated HCP molecule, where the r_s is smaller than the r_h. He also pointed out that the van der Waals (major and minor) radii of an atom in an isolated molecule can be predicted at the position where the electron density is 0·005 a.u. (0·0337 e Å^{-3}). These predicted radii of several atoms (F, Cl, Br, N, P, O and S atoms) in isolated molecules (Ikuta, 1989*a*,*b*) agree well with the values experimentally estimated by Nyburg & Faerman (1985).

The present paper describes the electron density distribution around an H atom in ten linear molecules (H_2, HF, HCl, HOLi, HONa, HCN, HCP, HBeH, HLi and HNa). The r_s and r_h values predicted in the present study will provide us with useful hints for considering the size of an H atom in molecules in the crystal, which is difficult to determine by X-ray crystal structure analysis.

2. Method

Geometry optimizations of linear molecules were performed with the Hartree–Fock level of theory using the 6-31G(*d*,*p*) basis sets (Hehre, Ditchfield & Pople, 1972; Hariharan & Pople, 1973; Gordon, 1980); the optimized geometries are shown in Fig. 1.

Electron density distributions around H atoms in molecules were calculated in two directions relating to r_s and r_h by using a Hartree–Fock level of theory with the 6-311G(2*d*,*p*) (Krishnan, Binkley, Seeger & Pople, 1980) or MC-311G(2*d*,*p*) (McLean & Chandler, 1980) basis sets. The basis-set dependency and the electron-correlation effect have already been reported to be negligible (Ikuta, 1989*b*; Boyd & Wang, 1989) if extended basis sets are used.

All the calculations were performed using the North-Dakota version of the *GAMESS* program (Dupuis, Spangler & Wendolski, 1981; Schmidt, 1989).

3. Results and discussion

Electron densities at various positions from the H nucleus in ten linear molecules, calculated in two (major and minor) directions, are listed in Table 1 and some of them are shown in Fig. 2 as a function of the distance from the H nucleus (*l*).

The densities decrease monotonously in both directions with increase of the distance *l*. The densities in the major direction are always greater than those in the minor one.

Calculated r_s and r_h radii of H atoms are summarized in Table 2; $r_s - r_h$ values, the Mulliken atomic charges on the H atom [δ(H)], and the electronegativity of substituent *X* [$\chi(X)$] (Pearson, 1988*a*,*b*) are also included. These results clearly indicate the presence of the anisotropy in both the electron density distribution and the van der Waals radii of the H atoms.

The r_s and r_h values in an H_2 molecule are 1·14 and 0·97 Å, respectively, the $r_s - r_h$ value being 0·17 Å. This value is comparable with that of the Cl atom in an HCl molecule (Ikuta, 1989*b*).

The r_s and r_h values in an HF molecule are different from the corresponding radii in HCl, whereas the $r_s - r_h$ (~0·33 Å) in both the molecules are equal to each other. These results suggest that the volumes of both the H atoms are different from each other reflecting the different electronegativity of substituent F and Cl atoms, but that the global shape of the distribution (the degree of the anisotropy) is similar in each case.

The r_s of the H atom in LiOH is 1·19 Å and that in NaOH 1·21 Å. On the other hand the r_h in LiOH is 0·86 Å and the value in NaOH is 0·88 Å. Thus the values of $r_s - r_h$ in these molecules are both 0·33 Å. These calculated results reflect the similar atomic charges on the H atoms in both molecules, indicating

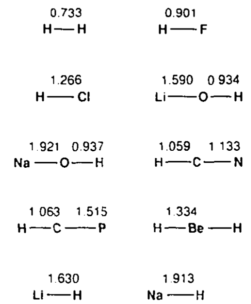


Fig. 1. Geometries optimized with the HF/6-31G(*d*,*p*) method. Bond lengths in Å.

Table 1. *Calculated electron densities at various positions from the* H *nucleus in ten linear molecules* (a.u.)

1a.u. = 6·7483 e Å^{-3}.

l* (Å)	Major direction	Minor direction	Major direction	Minor direction
	HF		HCl	
0·0	0·4048	0·4048	0·3621	0·3621
0·1	0·3079	0·2539	0·2785	0·2444
0·2	0·2106	0·1419	0·1951	0·1466
0·3	0·1485	0·0775	0·1361	0·0858
0·4	0·0946	0·0418	0·0949	0·0497
0·5	0·0630	0·0228	0·0666	0·0292
0·6	0·0416	0·0124	0·0465	0·0174
0·7	0·0274	0·0069	0·0322	0·0106
0·8	0·0177	0·0039	0·0222	0·0067
0·9	0·0115	0·0023	0·0154	0·0043
1·0	0·0074	0·0014	0·0106	0·0029
1·1	0·0047	0·0008	0·0074	0·0019
1·2	0·0029		0·0051	0·0013
1·3	0·0017		0·0036	0·0008
1·4	0·0010		0·0025	
	LiOH		NaOH	
0·0	0·4349	0·4349	0·4398	0·4398
0·1	0·3322	0·2818	0·3359	0·2871
0·2	0·2293	0·1630	0·2320	0·1676
0·3	0·1567	0·0927	0·1588	0·0963
0·4	0·1064	0·0525	0·1083	0·0552
0·5	0·0725	0·0303	0·0742	0·0323
0·6	0·0492	0·0178	0·0507	0·0191
0·7	0·0332	0·0106	0·0345	0·0116
0·8	0·0224	0·0065	0·0236	0·0072
0·9	0·0153	0·0042	0·0162	0·0046
1·0	0·0105	0·0027	0·0112	0·0030
1·1	0·0072	0·0018	0·0077	0·0020
1·2	0·0049	0·0011	0·0053	0·0013
1·3	0·0033	0·0007	0·0036	
1·4	0·0022		0·0024	
1·5	0·0015		0·0015	
	HCN		HCP	
0·0	0·4047	0·4047	0·4168	0·4168
0·1	0·3107	0·2724	0·3197	0·2821
0·2	0·2163	0·1631	0·2225	0·1702
0·3	0·1492	0·0954	0·1534	0·1006
0·4	0·1021	0·0550	0·1051	0·0589
0·5	0·0699	0·0320	0·0721	0·0349
0·6	0·0473	0·0188	0·0489	0·0209
0·7	0·0316	0·0111	0·0329	0·0127
0·8	0·0210	0·0068	0·0220	0·0079
0·9	0·0139	0·0042	0·0148	0·0051
1·0	0·0093	0·0027	0·0100	0·0033
1·1	0·0062	0·0018	0·0068	0·0022
1·2	0·0041	0·0011	0·0046	0·0014
1·3	0·0027	0·0007	0·0032	
1·4	0·0018		0·0022	
1·5	0·0012		0·0016	
1·6	0·0008		0·0011	
	H_2		BeH_2	
0·0	0·4012	0·4012	0·3786	0·3786
0·1	0·3084	0·2779	0·2919	0·2752
0·2	0·2146	0·1734	0·2056	0·1810
0·3	0·1475	0·1068	0·1446	0·1182
0·4	0·1003	0·0655	0·1018	0·0771
0·5	0·0680	0·0407	0·0724	0·0510
0·6	0·0457	0·0254	0·0514	0·0339
0·7	0·0304	0·0159	0·0364	0·0226
0·8	0·0201	0·0102	0·0258	0·0153
0·9	0·0134	0·0066	0·0184	0·0104
1·0	0·0089	0·0044	0·0132	0·0072
1·1	0·0059	0·0029	0·0095	0·0050
1·2	0·0039	0·0020	0·0068	0·0035
1·3	0·0026	0·0013	0·0048	0·0024
1·4	0·0017	0·0009	0·0034	0·0016
1·5			0·0024	0·0011
1·6			0·0017	0·0007
1·7			0·0012	
	LiH		NaH	
0·0	0·3250	0·3250	0·3097	0·3097
0·1	0·2511	0·2444	0·2393	0·2342
0·2	0·1777	0·1674	0·1694	0·1616
0·3	0·1260	0·1145	0·1203	0·1114
0·4	0·0898	0·0786	0·0859	0·0772
0·5	0·0649	0·0548	0·0622	0·0543
0·6	0·0471	0·0384	0·0453	0·0385
0·7	0·0343	0·0271	0·0331	0·0275
0·8	0·0252	0·0193	0·0241	0·0199
0·9	0·0186	0·0140	0·0182	0·0145
1·0	0·0139	0·0102	0·0137	0·0107
1·1	0·0105	0·0075	0·0104	0·0079
1·2	0·0079	0·0055	0·0079	0·0059
1·3	0·0059	0·0040	0·0060	0·0043
1·4	0·0045	0·0029	0·0046	0·0032
1·5	0·0034	0·0021	0·0035	0·0024
1·6	0·0027	0·0015	0·0027	0·0017
1·7	0·0020	0·0011	0·0021	0·0013
1·8	0·0015	0·0008	0·0016	0·0009

*Distance from the H nucleus.

that the effect of Li and Na atoms through the adjoining O atom on the electron density distribution around the H atom is quite small in these molecules.

The data on HCN and HCP molecules again indicate that the effect of N and P atoms through the adjoining C atom on the electron density distribution around the H atom is small.

The r_s and r_h values in LiH and NaH molecules are the largest among the present molecules. The values of $r_s - r_h$ in these molecules are 0·13 and 0·11 Å, respectively, the smallest in the present study. Thus the electron density distribution around the H atoms in the LiH and NaH molecules is only slightly flattened with polarity; the negative atomic charges on the H atom (−0·332 in LiH and −0·392 in NaH) indicate that the electrons flow into the H atoms and thus polar flattening becomes small. These results suggest that the electron density distribution around the H atom in a KH molecule approaches a spherical one.

The r_s, r_h and $r_s - r_h$ values are plotted in Fig. 3 as a function of δ(H). Both the r_s and r_h radii are

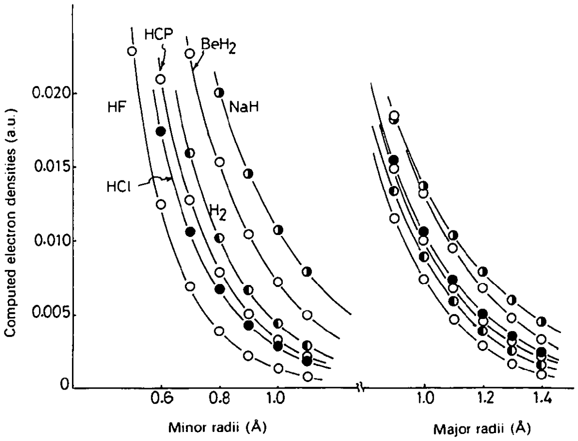


Fig. 2. Electron densities computed in the two directions plotted as a function of distance from the H nucleus.

Table 2. *Predicted major and minor radii in linear molecules* (Å)

HX molecule	r_s[a]	r_h[b]	$r_s - r_h$[c]	δ(H)[d]	$\chi(X)$[e]
HF	1·08	0·75	0·33	0·358	10·41
HCl	1·20	0·86	0·34	0·165	8·31
LiOH	1·19	0·86	0·33	0·211	
NaOH	1·21	0·88	0·33	0·196	
HCN	1·15	0·87	0·28	0·175	8·92
NCP	1·18	0·90	0·28	0·128	
H_2	1·14	0·97	0·17	0·000	7·17
BeH_2	1·28	1·10	0·18	−0·097	
LiH	1·35	1·22	0·13	−0·332	3·01
NaH	1·36	1·25	0·11	−0·392	2·85

Notes: (*a*) Major radii of H atoms. (*b*) Minor radii. (*c*) The difference between the major and minor radii (degree of anisotropy). (*d*) Mulliken atomic charges on H atom. (*e*) Electronegativity of X in HX molecules (in eV).

linearly related to δ(H); both the radii decrease with the increase of the positive charge on the H atom. The slope in the relation between r_h and δ(H) is steeper than that between r_s and the δ(H). In HX molecules, a more electronegative substituent X attracts more electrons from the H atom and thus a larger positive charge will be produced on the H atom. In the figure, the r_s in an H_2 molecule deviates somewhat from the linear relationship. With the decrease of δ(H), $r_s - r_h$ becomes small, and the electron distribution around the H atom becomes almost spherical. These straight lines suggest that one can estimate the van der Waals radii of H atoms in isolated linear molecules from δ(H).

In Fig. 4, the r_s, r_h and $r_s - r_h$ values are plotted against the electronegativity of X, $\chi(X)$ (Pearson, 1988*a*,*b*). Some of the $\chi(X)$ are not known at present and thus are not included in the figure. Although the data on H_2 somewhat deviate from the lines, linear relationships hold in all cases. An electronegative substituent X attracts the electrons from the H atom through the H—X σ bond in HX molecules and the r_h very much depends on $\chi(X)$.

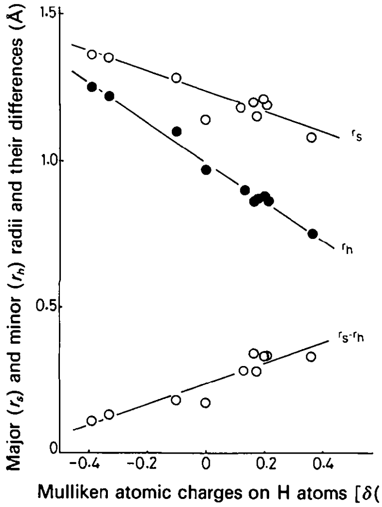


Fig. 3. Major (r_s) and minor (r_h) radii and the degree of anisotropy ($r_s - r_h$) plotted as a function of the Mulliken atomic charge on the H atom in the molecule.

The r_h value ranges from 0·75 Å (in HF) to 1·25 Å (in NaH); the difference amounts to 0·5 Å. On the other hand, the r_s ranges from 1·08 Å (in HF) to 1·36 Å (in NaH); the difference (0·28 Å) is about half of the above difference in the r_h. These results again indicate that the r_h strongly depends on the substituent X.

In Fig. 5 the correlation between the major and minor radii is examined. A good correlation exists between the two data sets, the slope being about 0·45. These results again indicate that polar flattening is present in the H atom in all the linear molecules and that the substituent X affects the r_h radius more effectively. Maximum polar flattening (0·33–0·34 Å) is observed in the H atoms of HF, HCl,

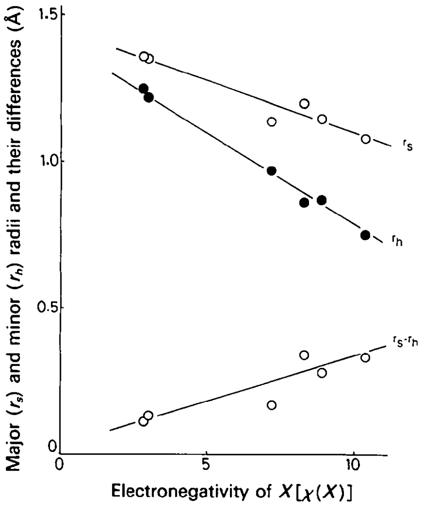


Fig. 4. Major (r_s) and minor (r_h) radii and the degree of anisotropy ($r_s - r_h$) plotted as a function of the electonegativity of X in linear HX molecules.

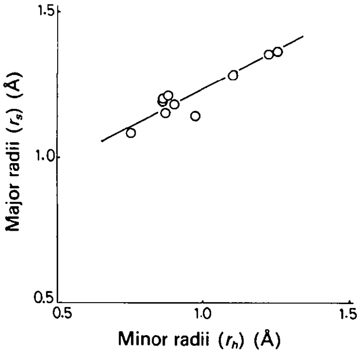


Fig. 5. Correlation between the major (r_s) and minor (r_h) radii.

LiOH and NaOH molecules, whereas minimum flattening (0·13–0·11 Å) is found in LiH and NaH molecules.

Of course one must account for the environment surrounding the isolated molecules if one wants to compare the present theoretical results with real systems in the crystals. Such theoretical approaches are now scheduled.

The authors thank Dr Michael Schmidt, North-Dakota State University, who kindly provided them with the North-Dakota version of *GAMESS* program. A special debt of gratitude goes to our mentors: Professor N. S. Hush and G. Bacskay, The University of Sydney, who introduced us to these areas.

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Bonding-Deformation and Superposition Effects in the Electron Density of Tetragonal Nickel Sulfate Hexadeuterate $NiSO_4.6D_2O$

BY G. J. MCINTYRE,* H. PTASIEWICZ-BAK† AND I. OLOVSSON

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21 *Uppsala, Sweden*

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Abstract

The electron density in the title compound has been determined at room temperature by multipole refinement against single-crystal X-ray intensity data. Hydrogen positional and displacement parameters were fixed to values determined by refinement against single-crystal neutron data. The electron density based on the deformation functions of all atoms in the structure is compared with the individual densities calculated from the deformation functions of only nickel or the separate water molecules. In this way the effects of simple superposition of the individual densities have been studied. The experimental deformation density around nickel is in good agreement with that expected from simple ligand-field theory for an ideally octahedral $Ni(D_2O)_6^{2+}$ complex. The individual densities of the water molecules show clear polarization of the lone-pair densities according to the coordination of the water molecules. This polarization is distorted by superposition in the electron density based on all atoms; in particular, the apparent decrease of the electron density in the lone-pair regions of the water O atoms can be attributed to superposition of the oxygen density with the negative deformation density of nickel. Crystal data: $NiSO_4.6D_2O$, $M_r = 274{\cdot}92$, $P4_32_12$, $a = 6{\cdot}7803\ (6)$, $c = 18{\cdot}288\ (2)$ Å, $V = 840{\cdot}73\ (2)$ Å^3, $Z = 4$, $T = 295$ K; $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 2{\cdot}553\ \text{mm}^{-1}$, $F(000) = 544$, $R = 0{\cdot}014$ for 1765 reflections (X-ray); $\lambda = 1{\cdot}210$ Å, $\mu = 0{\cdot}047\ \text{mm}^{-1}$, $R = 0{\cdot}035$ for 628 reflections (neutron).

1. Introduction

Experimental deformation electron densities of compounds comprising first- and second-row elements are mostly in good qualitative agreement with theoretical deformation maps (reviewed by Feil, 1986). For compounds with heavier elements, however, the picture is less clear. On the theoretical side it is unclear as to what extent the deformation is dominated by crystal-field effects, *i.e.* what exactly should

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* Present address: Institut Laue–Langevin, 156X, 38042 Grenoble CEDEX, France.

† Permanent address: Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.

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