Theoret. Chim. Acta (Berl.) 45, 121–126 (1977)

THEORETICA CHIMICA ACTA

Ab initio SCF MO Calculations on the CH_3Br Molecule

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Self-consistent field *ab initio* calculations have been performed for CH_3Br. The calculated equilibrium conformation is in good agreement with experiment. Valence and core level ionization potentials, Mulliken population analysis and electronic properties are presented. The ionization potentials are in good agreement with the experimental values, except for one case in which the experimental value may be wrongly assigned. The calculated dipole moment, 2.43 Debye, is 34% or 0.6 Debye larger than the experimental value.

Key words: CH_3Br

Ab initio calculations have been reported on CH_3F and CH_3Cl, the first two members of the methyl halide series [1, 2]. However, there have not been any theoretical results reported for the third member, methyl bromine. It appears desirable to have SCF wave functions for CH_3Br in order to compare the computed equilibrium geometry and other properties with experimental values. In particular, it is of importance to determine how well the LCAO-MO SCF method predicts properties of molecules containing heavy atoms.

In the present paper, we present some parameters of the calculated equilibrium geometry of CH_3Br. We have also determined valence and core level ionization potentials and compare these where possible with photoelectron spectra [3]. We report the values of some electronic properties that may be of interest to the experimental chemist. All the calculations were carried out using a double zeta basis set of contracted Gaussian basis functions.

For large molecules, it is desirable to explicitly vary as few geometrical parameters as possible in order to minimize the cost of the calculation. For CH_3Br, it appears that we may avoid variation of the C–H bond length. The experimental C–H bond lengths for CH_3X (X=F, Cl, Br) are 1.1050 Å, 1.0959 Å and 1.0954 Å [4] respectively. The experimental C–H bond lengths in the CHX (X=F, Cl) series are 1.121 Å [5] and 1.120 Å [6] respectively. Previous calculations [7] on the singlet states of CHF, CHCl and CHBr using a double zeta basis set gave optimum C–H bond lengths of 1.111 Å (CHF), 1.101 Å (CHCl) and 1.103 Å (CHBr). The agreement with the experiment is about 0.01 Å, and it is observed that the C–H bond length remains nearly constant in the CH_3X and CHX series. This led us to freeze the C–H bond length throughout the present calculations to its experimental value 1.0954 Å (2.07 a.u.).

The starting geometry for the C–Br variations was the experimental conformation [4]; C–Br = 1.9388 Å (3.6638 a.u.), C–H = 1.0954 Å (2.07 a.u.) and HCH = 111.63°. The C–Br bond length was varied until a minimum was reached and then the HCH angle was varied (using a C–Br bond length very close to the interpolated minimum), until a new minimum was reached.

The basis set exponents and contraction coefficients were those optimized by Dunning [8, 9] for the C, H, and Br atoms. The numbers of elementary and contracted functions are: C(9, 5/4, 2), H(4/2), and Br(15, 12, 5/8, 6, 2). The parameters of the basis set are given in Table 1. The energy for the Br atom with this basis

Table 1. Basis set exponents, α_i, and contraction coefficients, C_i; see Refs. [8] and [9]

Atom	Type	α_i	C_i	Atom	Type	α_i	C_i
Br	1*s*	439700.0	0.000813		4*p*′	0.1507	1.0
		66030.0	0.006285		3*d*	134.8	0.01831
		15140.0	0.03192			36.39	0.1350
		4317.0	0.1288			12.16	0.4261
		1414.0	0.3946			4.341	0.6043
		523.9	0.5413		3*d*′	1.535	1.0
	1*s*′	523.9	0.1831				
		207.7	0.6176	C	1*s*	4233.0	0.002029
		86.54	0.2538			634.9	0.01554
	2*s*	30.52	1.0			146.1	0.07541
	2*s*′	12.98	1.0			42.50	0.2571
	3*s*	4.412	1.0			14.19	0.5966
	3*s*′	1.862	1.0			1.967	0.2425
	4*s*	0.5455	1.0		1*s*′	5.148	1.0
	4*s*′	0.1902	1.0		2*s*	0.4962	1.0
	2*p*	2957.0	0.02226		2*s*′	0.1533	1.0
		700.3	0.1802		2*p*	18.16	0.01853
		224.6	0.8624			3.986	0.1154
	2*p*′	82.59	0.3440			1.143	0.3862
		33.19	0.5071			0.3594	0.6401
		14.20	0.2590		2*p*′	0.1146	1.0
	3*p*	14.20	0.07965				
		7.438	0.3734	H	1*s*	19.24	0.03283
		3.526	0.6049			2.899	0.2312
	3*p*′	1.595	1.0			0.6534	0.8172
	4*p*	0.4918	1.0		1*s*	0.1776	1.0

set is −2572.313 a.u. which compares favorably with the Hartree-Fock limit −2572.443 a.u. [10]. The use of only two contracted *p* functions on carbon does not seem to be a serious limitation. At one point near the computed equilibrium (HCH = 111.63° and C–Br = 3.7638 a.u.), we performed an SCF calculation using three *p* functions on carbon contracted (3, 1, 1) [8]. The resulting energy, −2611.9250 a.u., was only 0.0027 a.u. (0.07 eV) lower than that obtained with the double-zeta basis. These considerations give confidence in the basis set used in the present work. All SCF calculations were performed by using the joint MOLECULE/ALCHEMY SCF Program [11].

Table 2 gives the calculated total energies for the different C–Br bond lengths and HCH angles. The equilibrium conformation, calculated by parabolic interpolation to the three points nearest the minimum for each mode, is C–Br = 3.762 a.u. and HCH = 111.24°. The experimental values [4] are 3.6638 and 111.63° respectively. (The potential surface is extremely flat with respect to the C–Br distance and the HCH angle changes only slightly from the starting value. Thus, it was not necessary to re-optimize the C–Br distance using the optimized HCH angle.) It is observed that the bond length is somewhat longer than the experimental one. The HCH angle is in very good agreement with the experimental value. The C–Br stretching frequency, calculated via a parabolic fit to the C–Br bond length variations, is 602 cm^{-1}. This may be compared with the experimental stretching frequency (dominantly C–Br) of 611 cm^{-1} [12].

We now turn to a consideration of the ionization potentials, population analysis and other properties of CH_3Br. These results are all given for the following geometry: C–Br = 3.7638 a.u., C–H = 2.07 a.u. and HCH = 111.63°.

Table 3 shows the gross and overlap populations. The carbon atom appears to be negatively charged whereas the bromine atom is almost neutral. In a CH_4 calculation (at the experimental conformation) using the same basis set, the gross population of the C atom is 6.78. This shows that the polarizing effect of the Br atom in CH_3Br is very small. The C–H overlap population is larger than that for C–Br showing that the C–H bond is stronger as was expected.

Table 2. Calculated SFC energies for CH_3Br. The C–H bond length is 2.07 a.u.

C–Br (a.u.)	HCH (degrees)	Total energy (a.u.)
∞	–	−2611.490108[a]
3.6138	111.63	−2611.920115
3.6638	111.63	−2611.921364
3.7138	111.63	−2611.922062
3.7338	111.63	−2611.922201
3.7638	111.63	−2611.922270
3.7938	111.63	−2611.922181
3.7638	106.63	−2611.919288
3.7638	110.66	−2611.922244
3.7638	116.63	−2611.915512

[a] Sum of the separated atom SCF energies for $C(^3P)$, $Br(^2P)$, and $H(^2S)$

Table 3. Mulliken population analysis for CH_3Br

Atom	Gross population
C	6.69
Br	35.04
H	0.76
Bond	**Overlap population**
C—H	0.67
C—Br	0.47

Table 4 shows the first thirteen CH_3Br ionization potentials (*IP*'s) and relaxation energies (E_{relax}); experimental values are shown when available. There are two ways of computing the *IP*'s: a) From Koopmans' theorem, in which case, $IP(KT) = -\varepsilon_i$ where ε_i is the orbital energy of the *i*th MO. b) By subtracting the total SCF energy of the neutral species and the total energy of the ion; $IP(\Delta E_{\text{SCF}}) = E(\text{ion}) - E(\text{neutral})$. Then, $E_{\text{relax}} = IP(KT) - IP(\Delta E_{\text{SCF}})$.

It is observed from Table 4 that the first three *IP*'s are in reasonable agreement with the experimental values. (The first experimental *IP* is adiabatic (0-0 transition) and our calculated *IP* is vertical.) The fourth *IP* does not agree at all with the experimental value. An examination of the fourth orbital shows that it is a "localized C–Br bond like orbital" which gives support for the high calculated *IP*. The experimental third and fourth *IP* are very similar; however, the third orbital shows little resemblance to the fourth. These considerations make us believe that the fourth experimental *IP* is associated with the third electronic ionization. It may arise from vibrational excitation or Jahn-Teller splitting in the final (ionic) state.

Table 4. Calculated vertical ionization potentials, $IP(KT)$ and $IP(\Delta E_{\text{SCF}})$, and relaxation energies, $E_{\text{relax}} = IP(KT) - IP(\Delta E_{\text{SCF}})$, in eV (1 a.u. = 27.21165 eV). The principal atomic character of each molecular orbital is also given

	$IP(KT)$	$IP(\Delta E_{\text{SCF}})$	E_{relax}	*IP* (experiment)[a]
$6e(4p\text{Br})$	10.82	9.76	1.06	10.53
$10a_1(4p\text{Br} + 2p\text{C})$	13.32	12.37	0.95	13.52
$5e(4p\text{Br} + 2p\text{C} + 1s\text{H})$	16.60	15.25	1.36	15.14
$9a_1(4s\text{Br} + 2s\text{C})$	24.49	23.71	0.77	15.85
$8a_1(4s\text{Br} + 2s\text{C})$	28.65	27.75	0.90	
$4e(3d\text{Br})$	85.52	76.05	9.47	
$3e(3d\text{Br})$	85.81	76.32	9.49	
$7a_1(3d\text{Br})$	85.92	76.40	9.52	
$2e(3p\text{Br})$	201.63	192.44	9.18	
$6a_1(3p\text{Br})$	201.87	192.64	9.23	
$5a_1(3s\text{Br})$	266.78	257.54	9.23	
$4a_1(1s\text{C})$	307.36	293.30	14.05	
$1e(2p\text{Br})$	1591.27	1564.24	27.03	

[a] See Ref. [3]

Table 5. One-electron properties evaluated with respect to the Br atom. The dipole moment is in Debyes and all other properties are in atomic units

Property	
μ_z	2.43 Debye
E_z	-0.0535
F_{zz}	-8.2145
χ^d_{av}	-17.8385
$\chi^d_{xx}-\chi^d_{\text{av}}$	-1.4305
$\chi^d_{yy}-\chi^d_{\text{av}}$	-1.4305
$\chi^d_{zz}-\chi^d_{\text{av}}$	2.8610
θ_{zz}	4.2915

The relaxation energies increase, in general, as the *IP* increases. There are however some exceptions; the $3d$ orbitals in the Br atom have slightly higher relaxation energies than the $3p$ orbitals. It is interesting to compare the *IP*'s and relaxation energies of the $3p$ and $3d$ orbitals in CH_3Br with those found for the free Br atom. We have computed these atomic *IP*'s using an average of configuration [13] for the final states $3p^5 3d^{10} 4s^2 4p^5$ and $3p^6 3d^9 4s^2 4p^5$. (The atomic SCF calculations use the Gaussian basis set given for Br in Table 1.) The *IP*'s are 194.09 eV ($3p^{-1}$) and 78.36 eV ($3d^{-1}$); the relaxation energies being 8.68 eV and 8.42 eV respectively. This shows that the CH_3Br relaxation energies of these orbitals ($7a_1$, $4e$, $3e$ for $3d$ and $6a_1$ and $2e$ for $3p$) are mainly due to the atomic character of Br.

Table 5 gives the value of some one-electron properties of CH_3Br. All properties are evaluated with respect to the Br atom as origin and include both electronic and nuclear contributions. The co-ordinate system is chosen so that the z-axis is along the Br–C bond and points toward C. The calculated value of the dipole moment, $\mu_z = 2.43$ Debyes, is 34% larger than the experimental value [14] of 1.81. The diamagnetic susceptibility is presented as χ^d_{av} and $\chi^d_{\text{av}} - \chi^d_{gg}$ ($g = x, y, z$) as this is the most convenient form to compare with experimental values. The experimental data provide greater accuracy for the anisotropies in the diamagnetic susceptibility tensor than for the individual components [15]. We also present the non-zero component of the electric field, E_z, and the z^2 components of the field gradient, $F_{zz} = \langle (3z^2 - r^2)/r^5 \rangle$, and the quadrupole moment, $\theta_{zz} = \langle 3z^2 - r^2 \rangle / 2$.

In conclusion, the results of our calculations appear to give a reasonable description of CH_3Br. The calculated ionization potentials are in good agreement with the experimental values, except for one case in which there are grounds to believe that the assignment of the experimental *IP* is incorrect. The calculated equilibrium conformation is close to the observed geometry and the computed dipole moment is in error by 34%.

Two of us (C.W.B. and G. del C.) wish to acknowledge the hospitality of the IBM San José Research Laboratory and joint study agreements between the IBM and the Lawrence Berkeley Laboratory and the National University of Mexico respectively.

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Received October 27, 1976