

# Relativistic effects in physics and chemistry of element 105. II. Electronic structure and properties of group 5 elements bromides

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Relativistic self-consistent charge Dirac-Slater discrete variational method calculations have been done for the series of molecules  $MBr_5$ , where  $M = Nb, Ta, Pa$ , and element 105, Ha. The electronic structure data show that the trends within the group 5 pentabromides resemble those for the corresponding pentaclorides with the latter being more ionic. Estimation of the volatility of group 5 bromides has been done on the basis of the molecular orbital calculations. According to the results of the theoretical interpretation  $HaBr_5$  seems to be more volatile than  $NbBr_5$  and  $TaBr_5$ .

## I. INTRODUCTION

A very interesting chemical behavior of elements 104 and 105 compared to their analogs Zr, Hf and Nb, Ta, respectively, has been shown in the experiments on the volatility of their halides using the gas-chromatography technique. There are two groups of these gas-phase experiments. In the first case<sup>1-5</sup> reaction products are swept with a gas into the experimental set up which mainly consists of a quartz gas chromatography column with a temperature gradient along it. Short-lived isotopes of those elements are produced on line in a nuclear reaction at a heavy ion accelerator and the halides (chlorides or bromides) are formed by adding chlorinating or brominating agents. In the experiment the inner surface of the column serves as a track detector for fission fragments and the deposition temperature of compounds is correlated with sublimation enthalpies.

In the second series of experiments<sup>6-8</sup> on-line isothermal gas phase chromatography was applied to investigate the volatility of elements 104 and 105 bromides after transporting the reaction products with a He KCl-cluster jet to the quartz column. The bromides are formed after all clusters have been destroyed in a hot quartz wool plug. They pass through an empty isothermal chromatography column, and the temperature which gives 50% chemical yield of products at the outlet is measured. These  $T_{50\%}$  values are correlated with boiling points of those compounds and are considered as a measure of volatility.

According to the results of these experiments the halides of elements 104 and 105 behave in a different way compared to the analogs: the tetrachloride<sup>2</sup> and tetrabromide<sup>4,8</sup> of element 104 are obviously more volatile than analogs (estimated  $\Delta H_{\text{subl}}$  for  $ZrCl_4$ ,  $HfCl_4$ , and  $104Cl_4$  are 25.9, 25.7, and 21.5 kcal/mol, respectively,<sup>9</sup> and the

$T_{50\%}$  for  $104Br_4$  is about 200 °C lower<sup>8</sup> compared to  $HfBr_4$ ) while, in contrast, the element 105 pentahalides seem to be less volatile than pentahalides of Nb and Ta<sup>5-8</sup> (the  $T_{50\%}$  shift of element 105 pentabromide,  $HaBr_5$ , is about 130 °C to the region of higher temperatures compared to Nb and Ta pentabromides<sup>7</sup>).

These peculiarities in the behavior of the gaseous  $104Br_4$  and  $105Br_5$  compared to their analogs as well as interest in the electronic structure of these compounds have given impact to the relativistic molecular calculations of  $MBr_5$  species, where  $M = Nb, Ta, Pa$ , and Ha, presented in this paper. (Protactinium pentabromide has also been included both in the experimental and theoretical investigations due to the fact that properties of some protactinium compounds resemble those for the group 5 *d* elements.) This work is a continuation of our investigations of the physicochemical properties of group 5 elements (including Ha) halides.<sup>10</sup>

In Sec. II some details of the calculations within the framework of the relativistic Dirac-Slater discrete variational method (DS DVM) are given. Sec. III contains the results of the molecular orbital (MO) calculations and analysis of the electronic structure of  $MBr_5$  molecules. In Sec. IV an attempt has been made to estimate the volatility of  $HaBr_5$  in comparison with analogs and to interpret the results of the gas-phase chromatography experiments.<sup>6-8</sup>

## II. METHOD OF THE CALCULATIONS

Calculations of the molecular electronic structure of  $MBr_5$  have been done using DS DVM with self-consistent charge (SCC) approximation.<sup>11</sup> The description of the method is given elsewhere.<sup>10</sup>

The calculations have been done both within the all-electron and the frozen core approximations in which symmetry orbitals are constructed for the core and valence regions.

The extended basis set including valence  $np_{1/2}$  and

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TABLE I. Input geometrical parameters: bond distances  $R_{M-Br}$  and  $Br_{ax}-M-Br$  angle ( $C_{4v}$ ) for  $MBr_5$ .

		Nb	Ta	Ha <sup>a</sup>	Pa <sup>a</sup>	Reference
	Symmetry	$D_{3h}$	$D_{3h}$	$D_{3h}$	$C_{4v}$	
(i)	$R_{M-Br}$ (Å)	2.46	2.45	2.54; 2.51	2.59 (105°)	13
(ii)	$R_{M-Br_{ax}}$ (Å)	2.46 <sup>a</sup>	2.473	2.55; 2.52 <sup>b</sup>	2.59 (105°)	14
	$R_{M-Br_{eq}}$ (Å)	2.43 <sup>a</sup>	2.412	2.49; 2.46 <sup>b</sup>	2.59	

<sup>a</sup>Estimated values (this work).

<sup>b</sup>Bond length with relativistic contraction.

$np_{3/2}$  orbitals was used to examine the influence of these orbitals on the chemical bond formation. The results on the charge density distribution presented in the paper are for the neutral basis set. The trends in these values within the group are the same for the ionized basis. Numerical integration was done using 9000 integration points.

Mulliken population analysis has been used to analyze the charge density distribution data.<sup>12</sup> The details of this analysis are given in Ref. 10.

### III. RESULTS AND DISCUSSION

#### A. Geometrical configurations of $MBr_5$ molecules ( $M=Nb, Ta, Ha, and Pa$ )

Electron diffraction studies<sup>13</sup> of the vapors indicated that the pentabromides of Nb and Ta are monomeric trigonal bipyramids with mean metal–bromine bond length of 2.46 Å in the niobium case and 2.45 Å for tantalum. In a later work<sup>14</sup> it was shown that the axial bonds in  $TaBr_5$  were longer than the equatorial ones by 0.061 (10) Å. These data together with estimated values are shown in Table I.

Interatomic distance  $Ha-Br$  has been varied from 2.40–2.60 Å in a series of calculations to check the sensitivity of this parameter. The results are mainly presented for  $R_{ax}/R_{eq} = 2.55/2.49$  Å, which have been assumed taking into account values of ionic radii obtained in multiconfiguration Dirac–Fock method (MCDF) atomic calculations,<sup>15</sup> and for  $R_{ax}/R_{eq} = 2.52/2.46$  Å, which could be realized in the case of relativistic bond contraction.<sup>10</sup> By analogy with  $PaCl_5$  (see Ref. 10), protactinium pentabromide was assumed to have  $C_{4v}$  symmetry. The bond lengths for  $PaBr_5$  were estimated on the basis of solid-state structural data.<sup>16</sup>

#### B. Energy level structures

Table II contains molecular orbital energies and in Fig. 1 the energy level structure is shown as a result of the calculations.

The pentabromides of Nb, Ta, and Ha have energy level structures similar to the corresponding pentachlorides.<sup>10</sup> The last occupied levels are MOs of predominantly  $4p$  character of Br. The  $d$  levels of the metal are separated from the set of binding levels by an energy gap  $\Delta E$ . The scheme of the  $d$  orbital splitting in the  $D_{3h}$  crystal field is preserved for all the molecules. The energy gap increases in going from  $NbBr_5$  to  $TaBr_5$  and to  $HaBr_5$  from 2.03 to 2.45 and to 2.71 eV, respectively. Compared to the correspond-

ing chlorides of Nb, Ta, and Ha this value decreases owing to higher energies of the valent  $4p$ (Br) orbitals compared to  $3p$ (Cl). This will result in the lower energies of the electronic charge-transfer transitions in  $MBr_5$  compared to analogous  $MCl_5$ . The crystal-field splitting of the  $d$  orbitals in  $MBr_5$  is about 0.5–0.8 eV less than that of  $MCl_5$  and increases from  $NbBr_5$  to  $TaBr_5$  and to  $HaBr_5$ .

#### C. Molecular orbital composition and bonding

The molecular orbital composition and bond orders for  $HaBr_5$  are given in Ref. 17. The six highest occupied molecular orbitals of  $4p$ (Br) character (48D7–43D9) are nearly nonbonding in nature and below them are orbitals with a little admixture of  $7p$  and  $6d$  orbitals of Ha. There are five orbitals responsible for the bonding with participation of  $6d$  atomic orbital(s) (AOs) of  $Ha(46D7-40D9)$  and the 45D7 orbital with participation of the  $7s$ (Ha) AO. Energetically below these levels are nearly pure atomic  $4s_{1/2}$  orbitals of Br and further down are pure atomic  $5f$  AOs of Ha. Compared to  $HaCl_5$  (see Ref. 10) there is higher contribution of  $6d$ ,  $7p$ , and especially  $7s_{1/2}$  orbitals to bonding.

The Mulliken analysis data on electron density distribution are shown in Table III. Compared to the analogous pentachlorides<sup>10</sup> the pentabromides of the group 5 elements have lower effective charges and higher populations of all the metal valence AOs. Along the series the values of  $Q$  and  $q_i$  change in the same way as in the case of the chlorides: the effective charges on Nb and Ta are nearly the same (Ta has by 0.005 higher value), Ha has a substantially lower effective charge, and Pa has the largest value of  $Q$ .

Relativistic AO populations are shown in Table IV. Differences in the  $Ha-Br$  bond lengths of 0.08 Å do not change much the charge density distribution in  $HaBr_5$ . One can see from Table IV that there is a gradual stabilization of  $ns_{1/2}$  and  $np_{1/2}$  AOs as a function of atomic number and thus the increase in their populations. The  $(n-1)d$  orbitals show destabilization with increasing atomic number and destabilization of  $(n-1)d_{3/2}$  AOs is not a smooth function of it. As in the case of the corresponding pentachlorides of Nb, Ta, and Ha (Ref. 10) the behavior of the  $np_{3/2}$  orbital is the most interesting one. In  $TaBr_5$  this is a relatively stabilized orbital while in  $HaBr_5$  its relative destabilization results in the overlap of  $7p_{3/2}$  orbital with ligands being the smallest in the series. So for the series of molecules under consideration the valent AOs contribute

TABLE II. Molecular orbital energies for  $MBr_5$ .

$NbBr_5$		$TaBr_5$		$HaBr_5$			
2.46/2.43 Å		2.47/2.41 Å		2.47/2.41	2.52/2.46	2.55/2.49 Å	
Orbital energy (eV)		Orbital energy (eV)		Orbital			
				Energy (eV)			
39D7	2.19	45D7	1.45	51D7	1.11	1.52	1.76
35D9	4.05	44D8	3.47	49D8	2.84	3.04	3.17
39D8	4.08	40D9	3.59	45D9	2.92	3.15	3.28
34D9	4.98	39D9	4.42	44D9	3.98	4.17	4.29
38D7	5.11	44D7	4.67	50D7	4.33	4.50	4.60
33D9	7.14	38D9	7.11	43D9	7.22	7.21	7.21
37D7	7.31	43D7	7.30	49D7	7.41	7.40	7.40
38D8	7.52	43D8	7.50	48D8	7.54	7.54	7.54
32D9	7.59	37D9	7.54	42D9	7.64	7.58	7.55
37D8	7.80	42D8	7.80	47D8	7.91	7.87	7.84
36D7	8.02	42D7	8.08	48D7	8.05	8.12	7.97
36D8	8.75	36D9	8.89	41D9	8.73	8.73	8.59
31D9	8.84	41D8	8.86	46D8	8.78	8.74	8.65
35D8	8.95	40D8	9.05	45D8	9.19	9.17	9.03
30D9	9.72	35D9	9.71	40D9	9.71	9.54	9.43
29D9	9.79	34D9	9.84	39D9	9.94	9.78	9.71
35D7	9.81	39D8	9.96	44D8	9.94	9.91	9.76
34D8	9.93	41D7	9.83	47D7	9.97	9.94	9.66
34D7	10.06	40D7	10.00	46D7	10.23	10.09	10.00
33D7	10.18	39D7	10.69	45D7	11.32	11.26	11.22
33D8	20.39	38D8	20.33	43D8	20.43	20.36	20.32
32D7	20.59	38D7	20.57	38D9	20.79	20.71	20.65
28D9	20.80	33D9	20.90	44D7	20.81	20.68	20.61
32D8	20.82	37D8	20.98	42D8	20.99	20.88	20.80
31D7	21.15	37D7	21.33	43D7	21.47	21.27	21.16
27D9	37.99	36D7	26.18	41D8	24.45	24.59	24.68
31D8	38.06	36D8	26.12	42D7	24.66	24.80	24.90
30D8	40.16	35D7	26.19	37D9	24.83	24.98	25.08
30D7	62.20	32D9	26.17	41D7	24.84	25.00	25.10

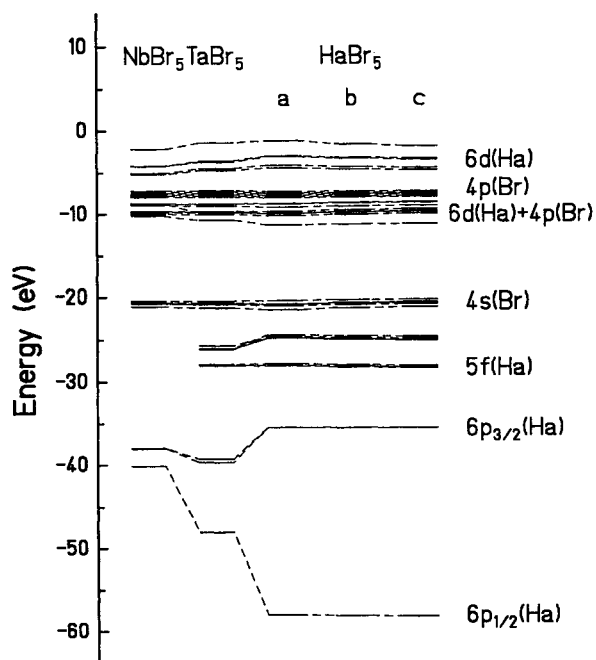


FIG. 1. Molecular orbital energies for  $MBr_5$ , where  $M=Nb, Ta,$  and  $Ha$  ( $a-R_{ax}/R_{eq} = 2.47/2.41$  Å,  $b-R_{ax}/R_{eq} = 2.52/2.46$  Å, and  $c-R_{ax}/R_{eq} = 2.55/2.49$  Å).

in a varying way to the bonding, nevertheless the total overlap between metal atom and the halogens steadily increases in going from  $NbBr_5$  to  $HaBr_5$  (Table V). Compared to the corresponding pentachlorides of the group 5 elements<sup>10</sup> the pentabromides show higher overlap population values and hence higher covalency. As in case of the pentachlorides there is an increase in covalency to a large extent from  $NbBr_5$  to  $TaBr_5$  and to a much less extent from  $TaBr_5$  to  $HaBr_5$ . The ionic and covalent contributions to the chemical bonding are given in Table V.

TABLE III. Effective charges on atoms ( $Q$ ) and atomic orbital populations ( $q_i$ ) for  $MBr_5$ .

Molecule	$R_{M-Br_{ax}}$ (Å)	$R_{M-Br_{eq}}$ (Å)	$Q$	$q_s$	$q_p$	$q_d$	$q_f$	$\Delta E$ (eV)
$NbBr_5$	2.46		0.69	0.27	0.28	3.77	...	2.03
	2.43							
$TaBr_5$	2.47		0.69	0.46	0.39	3.46	13.99	2.45
	2.41							
$HaBr_5$	2.47		0.53	0.61	0.38	3.48	13.99	2.86
	2.41							
$HaBr_5$	2.52		0.52	0.66	0.39	3.42	13.99	2.71
	2.46							
$HaBr_5$	2.55		0.51	0.68	0.40	3.38	13.99	2.59
	2.49							
$PaBr_5$	2.59		0.72	0.21	0.20	2.19	1.68	1.92

TABLE IV. Relativistic atomic orbital populations ( $q_j$ ) for  $MBr_5$ .

Orbital	NbBr <sub>5</sub>	TaBr <sub>5</sub>	HaBr <sub>5</sub>	HaBr <sub>5</sub>	HaBr <sub>5</sub>
			2.47/2.41 Å	2.52/2.46 Å	2.55/2.49 Å
$q_{s_{1/2}}$	0.27	0.46	0.61	0.66	0.68
$q_{p_{1/2}}$	0.10	0.18	0.25	0.26	0.27
$q_{p_{3/2}}$	0.18	0.21	0.13	0.13	0.13
$q_{d_{3/2}}$	1.59	1.53	1.63	1.62	1.61
$q_{d_{5/2}}$	2.18	1.93	1.85	1.80	1.77

Lower effective charges and larger overlap populations in the bromides compared to the corresponding chlorides are indicative of their higher covalency. The change in the chemical bond strength should have the same tendency as in the case of the chlorides. Thus in TaBr<sub>5</sub> compared to NbBr<sub>5</sub> there is an increase both in ionic and covalent contributions. This makes one believe that the Ta compound is less easily dissociated than the Nb one. In HaBr<sub>5</sub> compared to TaBr<sub>5</sub> the slight increase in the covalent part of the dissociation energy is partially compensated by a lower ionic contribution giving rise to possibly no extra stabilization of the Ha compound compared to the Ta one or resulting in an even lower stability. All these differences in dissociation energies will probably be few electronvolts only.

Ionization potentials for  $MBr_5$  molecules calculated via the transition state procedure are presented in Table V.

#### IV. VOLATILITY OF THE PENTABROMIDES

##### A. Volatility in its classical thermodynamical understanding

Identification of the properties of the transactinide elements by studying their volatility is a difficult task due to the fact that even for the lighter elements volatility is a property which is hardly correlated with one or even with a set of parameters. Available experimental data on volatility of different compounds are often contradictory and attempts to find direct correlation between electronic structure of the compounds and their volatilities are often speculative.

In macrochemistry volatility is determined through the Maxwell equation, connecting volatility, volume, temperature, and entropy of a substance. An approximate expression for the volatility as  $\ln P$  has the form

TABLE V. Mulliken analysis<sup>a</sup> data and ionization potentials ( $I$ ) for  $MBr_5$ .

Parameter	NbBr <sub>5</sub>	TaBr <sub>5</sub>	PaBr <sub>5</sub>	HaBr <sub>5</sub>	HaBr <sub>5</sub>
				2.52/2.46 Å	2.55/2.49 Å
$n(k)$	38.79	70.18	89.46	103.22	103.23
$Q_M$	0.69	0.69	0.72	0.52	0.51
$Q_{Br_{ax}}$	-0.15	-0.16	-0.17	-0.13	-0.13
$Q_{Br_{eq}}$	-0.13	-0.12	-0.14	-0.09	-0.09
$p_i$	0.08	0.10	0.11	0.05	0.05
$n_c$	2.26	2.69	2.07	2.76	2.78
$I$ (eV)	9.73	9.72	9.80	9.82	9.81

<sup>a</sup> $n(k)$ —total net atomic population;  $Q$ —effective atomic charge;  $n_c$ —covalent bond order (overlap population);  $p_i$ —ionic bond order equal to  $-\sum Q(k)Q(I)(a_0/R)$ .

$$\ln P = A - \frac{H_0}{RT} + \frac{\Delta c_p}{R} \ln T. \quad (1)$$

Here  $H_0$  is the sublimation enthalpy at the absolute zero temperature and  $\Delta c_p$  is the difference in specific heat of solid state and vapor.

In reality the more simple expression

$$\ln P = A - B/T \quad (2)$$

is used for volatility, where coefficients  $A$  and  $B$  are determined experimentally. Only temperature dependence of the vapor pressure can give information about volatility of a substance while the sublimation enthalpy and the temperature of sublimation are the reference parameters.

Homologs of HaBr<sub>5</sub>—NbBr<sub>5</sub> and TaBr<sub>5</sub>—are rather volatile compounds. They have molecular (dimeric) structure in solid state with the metal atoms screened by the halogens.

Although from various experiments there is a wide range of values given for the melting points of the pentabromides, there is reasonably good agreement about their boiling points, which show that TaBr<sub>5</sub> boils at 20 °C lower temperature than NbBr<sub>5</sub>. These physicochemical data<sup>18</sup> for NbBr<sub>5</sub> and TaBr<sub>5</sub> together with those for NbCl<sub>5</sub> and TaCl<sub>5</sub> (including data<sup>16</sup> for PaCl<sub>5</sub> and PaBr<sub>5</sub>) are shown in Table VI.

From chemical experiments<sup>13,19</sup> the following forms of Eq. (2) for the temperature dependence of the vapor pressure for NbBr<sub>5</sub> have been derived

$$\text{Solid } \log P_{mm} = 12.5 - \frac{5782}{T}, \quad (205\text{--}252 \text{ }^\circ\text{C})$$

TABLE VI. Physicochemical data (Ref. 18) for  $MBr_5$  and  $MCl_5$ .

Molecule	$T_m$ (°C)	$T_b$ (°C)	$\Delta H_s$ (kcal/mol)	$T_{50\%}^a$ (°C)	Molecule	$T_m$ (°C)	$T_b$ (°C)	$\Delta H_s$ (kcal/mol)
NbBr <sub>5</sub>	254	365	27.70	200	NbCl <sub>5</sub>	203.4	247.4	21.27
TaBr <sub>5</sub>	256	344	25.30	200	TaCl <sub>5</sub>	215.9	232.9	20.41
HaBr <sub>5</sub>	...	...	...	320	HaCl <sub>5</sub>	...	...	...
PaBr <sub>5</sub> <sup>b</sup>	283	428	24.60	...	PaCl <sub>5</sub> <sup>b</sup>	281.0	395.0	22.18

<sup>a</sup>Partly preliminary data (Refs. 6–8) which have to be confirmed in future experiments.

<sup>b</sup>Reference 16.

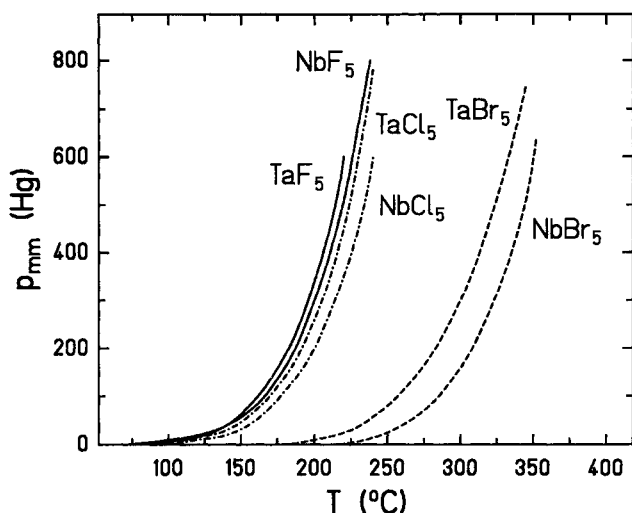


FIG. 2. Volatility of  $MF_5$  (solid lines),  $MCl_5$  (dashed-dotted lines), and  $MBr_5$  (dashed lines) molecules, where  $M=Nb$  and  $Ta$ , as a function of the temperature.

$$\text{Liquid } \log P_{mm} = 9.78 - \frac{4743}{T}, \quad (252-356^\circ\text{C}) \quad (3)$$

and for  $TaBr_5$

$$\begin{aligned} \text{Solid } \log P_{mm} &= 12.5 - \frac{5546}{T}, \quad (180-255^\circ\text{C}) \\ \text{Liquid } \log P_{mm} &= 8.07 - \frac{3204}{T}, \quad (255-344^\circ\text{C}). \end{aligned} \quad (4)$$

Graphically, Eqs. (3) and (4) along with analogous ones for  $MF_5$  and  $MCl_5$  are shown in Fig. 2. The volatility of the species decreases from the fluorides to the chlorides and to the bromides, and in all cases the tantalum halides are more volatile than the niobium ones. In the temperature interval between 180 and 320 °C, the vapor pressure of  $TaBr_5$  is a factor of 1.5–2 higher than that of  $NbBr_5$ .

In the area of low temperatures and low pressure  $A_{NbBr_5} = A_{TaBr_5}$ , and the relation between vapor pressures of  $NbBr_5$  and  $TaBr_5$  can be expressed in the following way

$$\log \frac{P_{NbBr_5}}{P_{TaBr_5}} = -\frac{B_{TaBr_5}(1-\gamma)}{T}, \quad (5)$$

where  $\gamma = B_{NbBr_5}/B_{TaBr_5}$ .

Let us assume that  $\gamma$  is determined by attraction energy between two identical molecules ( $NbBr_5$  and  $NbBr_5$  or  $TaBr_5$  and  $TaBr_5$ ). This dispersion interaction has the energy<sup>20</sup>

$$\epsilon(x) = -\frac{3}{4} \frac{h\nu_0 \alpha_1 \alpha_2}{x^6}, \quad (6)$$

where  $h\nu_0$  denotes the characteristic (roughly, ionization) energies for the two molecules or atoms,  $\alpha_1$  and  $\alpha_2$  are their polarizabilities, and  $x$  is the distance between the molecules or atoms.

If we suppose that the two  $MBr_5$  molecules interact via the two adjacent bromine atoms,  $\gamma$  could be expressed in the following way using Eq. (6)

$$\gamma = \frac{\epsilon(x)_{NbBr_5}}{\epsilon(x)_{TaBr_5}} = \frac{I_{Br}^{NbBr_5} (\alpha_{Br}^2)_{NbBr_5}}{I_{Br}^{TaBr_5} (\alpha_{Br}^2)_{TaBr_5}}, \quad (7)$$

where  $I_{Br}$  is ionization potential and  $\alpha_{Br}$  is polarizability of the bromine atom in a molecule.

Polarizability of a spherically symmetric atom is expressed as a cube of mean radius  $r$  of its electron shell

$$\alpha = \frac{4\pi}{3} r_{Br}^3. \quad (8)$$

Thus

$$\gamma = \frac{I_{Br}^{NbBr_5} (r_{Br}^6)_{NbBr_5}}{I_{Br}^{TaBr_5} (r_{Br}^6)_{TaBr_5}}.$$

For the bromine atom  $r = 1.14 \text{ \AA}$  and for the ion  $Br^-$   $r = 1.98 \text{ \AA}$ . So within the interval between effective charges  $Q=0$  and  $Q=-1$  the bromine radius changes according to

$$r_{Br}(Q) = 1.14 - 0.85Q, \quad (Q < 0). \quad (9)$$

Analogously the dependence of the ionization potential of the bromine atom on the effective charge can be expressed as

$$I_{Br}(Q) = 273 + 194Q \text{ (kcal)}, \quad (Q < 0). \quad (10)$$

Here 273 kcal is ionization potential ( $I$ ) of a neutral bromine and  $I - EA = 194$  kcal, where  $EA = 79$  kcal is the electron affinity of the bromine.

Finally  $\gamma$  as a dependence on effective charge  $Q$  has a form

$$\gamma = \frac{173 + 194Q_{Br}^{NbBr_5}}{173 + 194Q_{Br}^{TaBr_5}} \left( \frac{1.14 - 0.85Q_{Br}^{NbBr_5}}{1.14 - 0.85Q_{Br}^{TaBr_5}} \right)^6. \quad (11)$$

An increase in  $|Q|$  results in the decrease in  $I_{Br}$  and an increase in polarizability of the bromine atom due to an increase in  $r$ . Experimentally  $\log P_{NbBr_5}/P_{TaBr_5} = 1.04$ , which means stronger dispersion interaction for  $NbBr_5$  and lower vapor pressure. Using mean values of  $\langle Q \rangle_{Br}$  in  $NbBr_5$  and  $TaBr_5$  of the present molecular calculation (Table V) gives  $\gamma = 1$ . For the relation  $\log P_{TaBr_5}/P_{HaBr_5}$ , Eq. (11) gives  $\gamma = 1.09$ . Thus  $HaBr_5$  molecules should have weaker dispersion interaction and higher vapor pressure compared to  $TaBr_5$  at any fixed temperature. Taking into account the latter relation we find  $B_{HaBr_5} = 5088$ . Assuming that within the temperature range between 200 and 250 °C  $\log P_{HaBr_5}$  has a form similar to Eqs. (3) and (4); the dependence of  $\log P$  on  $T$  can be expressed as

$$\log P_{HaBr_5} = 12.5 - 5088/T, \quad (200-250^\circ\text{C}). \quad (12)$$

The plot  $P_{mm}(\text{Hg})$  vs  $T$  [Eq. (12)] for  $HaBr_5$  is shown on Fig. 3.

Besides the dispersion interaction some other parameters should be taken into account when estimating the vol-

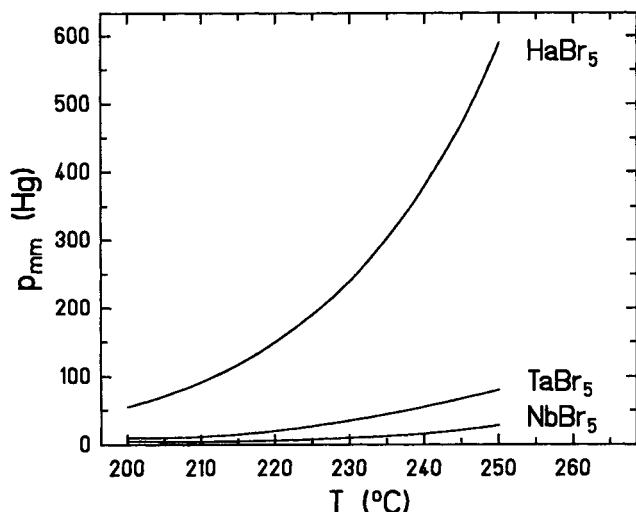


FIG. 3. Volatility of HaBr<sub>5</sub> in comparison with NbBr<sub>5</sub> and TaBr<sub>5</sub> within the temperature interval 200–250 °C.

atility of a substance. In the process of sublimation from solid state to gas the type of bonding both in the solid state and in the gas phase should be considered. It is known for example that for crystals of intermediate ionicity where each anion is surrounded by cations, an increase in covalency has no great influence on the lattice energy where all the forces are in equilibrium due to symmetry. Nevertheless in the gas phase the higher covalency facilitates stability of the system and decreases sublimation enthalpies or increases the solubility in nonpolar solvents. Assuming that in the solid state HaBr<sub>5</sub> has the same structure as NbBr<sub>5</sub> and TaBr<sub>5</sub>, the overlap population data ( $n_c$  from Table V), which are the measures of covalency of MBr<sub>5</sub> in a molecular state, can be used for the additional judgement about the volatility. Again HaBr<sub>5</sub> should be the most volatile species because of the highest covalency and PaBr<sub>5</sub> the least volatile one because of the lowest covalency (or overlap population).

### B. Volatility as it is measured in the gas-phase chromatography experiments

Volatility as it was determined in the experiments<sup>7,8</sup> (described in Sec. I), when only one atom at a time is produced, followed by the formation of a molecule, which is then investigated, is obviously a process of adsorption-desorption of these individual molecules on the surface of the chromatography column [in the experiments<sup>6-8</sup> the surface is believed to be totally or partially KBr (or KCl) from the deposition of the carrying cluster material on cooler parts of the surface of the quartz tube]. By breaking the interaction of a molecule with a surface into its constituents we try to estimate any particular interaction using data of the molecular calculations.

According to the particular type of symmetry of the adsorbate molecules, we suppose that the adsorption of MBr<sub>5</sub> molecules on the surface occurs via the interaction of the axial bromine atom with a bromine atom of the surface.

One could think of the following possible kinds of this interaction: (1) dispersion interaction of the bromine atom of the molecule with the bromine atom of the surface (at comparatively large  $x_0$  distances); (2) induction interaction energy contribution due to the additional polarization of the molecule (or the bromine atom) by the electric field of the surface; (3) Coulomb interaction with the positively charged metal atoms of the surface; or (4) the covalent bonding with a charge transfer.

It was observed experimentally<sup>7</sup> that in the process of adsorption of MBr<sub>5</sub> molecules on different surfaces of the chromatography column (SiO<sub>2</sub>, NiBr<sub>2</sub>, NaBr, KBr, CsBr) the  $T_{50\%}$  increases in direction from SiO<sub>2</sub> to CsBr. Assuming that ionicity of the surface increases in the same direction (thus for compounds with the same structure as NaCl the effective charges are Na<sup>+0.56</sup>Br<sup>-0.56</sup> and K<sup>+0.62</sup>Br<sup>-0.62</sup>) one can suppose a number of possible models of adsorption.

Let us consider the interaction of a particular molecule (e.g., NbBr<sub>5</sub>) with NaBr and KBr surface. The relation between the dispersion interactions of Br in NbBr<sub>5</sub> with the bromine atom of the NaBr surface and Br in NbBr<sub>5</sub> with a bromine of the KBr surface according to the model considered in Sec. IV A [Eqs. (7) and (8)] is

$$\gamma = \frac{I_{\text{Br}}^{\text{KBr}}(\alpha_{\text{Br}})^{\text{KBr}}(\alpha_{\text{Br}})^{\text{NbBr}_5}}{I_{\text{Br}}^{\text{NaBr}}(\alpha_{\text{Br}})^{\text{NaBr}}(\alpha_{\text{Br}})^{\text{NbBr}_5}} = \frac{I_{\text{Br}}^{\text{KBr}}(r_{\text{Br}}^3)^{\text{KBr}}}{I_{\text{Br}}^{\text{NaBr}}(r_{\text{Br}}^3)^{\text{NaBr}}} = 1.01. \quad (13)$$

This means that the dispersion interaction of the bromine atom of the NbBr<sub>5</sub> molecule with the bromine atom of the KBr surface is stronger compared to interaction of the bromine atom of the NbBr<sub>5</sub> molecule with the bromine atom of the NaBr surface. Induction interaction is also stronger in case of the KBr surface because KBr has a stronger electric field than NaBr.

In the case of the Coulomb interaction of a MBr<sub>5</sub> molecule with the surface, its strength will increase from NaBr to KBr due to the increase in effective charges from Na to K. The donor-acceptor interaction (or the charge transfer) increases from NaBr to KBr due to an increase in the differences between effective charges on Br in a MBr<sub>5</sub> molecule and the Br of the surface in going from NaBr to KBr. Thus the stronger interaction of a MBr<sub>5</sub> molecule with a more ionic surface can be explained within the considered models as a result of the stronger dispersion, induction, Coulomb or donor-acceptor interactions.

Applying now the same approach to the interaction of different MBr<sub>5</sub> molecules (M=Nb, Ta, Pa, and Ha) with one specific surface one can analyze these different interactions in the following way. The dispersion interaction of bromine atoms in MBr<sub>5</sub> molecules with the surface (e.g., KBr) decreases in the sequence PaBr<sub>5</sub>, NbBr<sub>5</sub>, TaBr<sub>5</sub>, and HaBr<sub>5</sub> due to decrease in polarizability of the bromine atom from Pa to Ha molecule. Due to the same reason the induction interaction energy decreases in this direction. The Coulomb interaction decreases in this direction due to the decrease in effective charges on the metal atoms in MBr<sub>5</sub>. Donor-acceptor interaction also decreases in going from PaBr<sub>5</sub> to HaBr<sub>5</sub> due to the decrease in the differences

between effective charges on Br atoms in  $MBr_5$  ( $M=Pa, Nb, Ta, \text{ and } Ha$ ) and the Br of the surface ( $KBr$ ).

Thus in the framework of the assumed models the interaction of the  $HaBr_5$  molecule with a particular surface should be the smallest in the series of the molecules under consideration and, hence, the volatility should be the highest.

One can see that the picture of the adsorption is very complicated even for the proposed model when the adsorption of  $MBr_5$  molecule occurs via the axial bromine atom. Calculations of the bonding of these molecules with the surface are needed for quantitative estimation of the adsorption. Nevertheless even within the proposed model it is difficult to find an explanation for the higher adsorption (or lower volatility) of  $HaBr_5$  molecules compared to those of  $Nb$  and  $Ta$  as observed in the experiments.<sup>7</sup>

Finally comparing groups 4 and 5 one can see that the elements of these groups should have in principal similar tendencies in the physicochemical properties, because such characteristics as ionic radii, energetic atomic structure, ionization potentials, etc., are quite similar for these two groups. Calculations<sup>9</sup> of the electronic structure of  $MCl_4$  ( $M=Zr, Hf, \text{ and } 104$ ) in terms of SCF- $X_\alpha$  scattering wave Dirac-Slater method have yielded the lower effective charge of 104 compared to  $Zr$  and  $Hf$ . This low effective charge was assumed to be a reason for the higher volatility of  $104Cl_4$  compared to  $ZrCl_4$  and  $HfCl_4$ . From our present theoretical studies, which are somewhat preliminary, of the group 4 elements we would conclude that the trends in volatilities within the groups 4 and 5 elements should be similar. A more detailed comparison has to await more careful studies of the electronic structure and related properties of the group 4 elements.

## V. CONCLUSIONS

The electronic structure data of  $MBr_5$  where  $M=Nb, Ta, \text{ and } Ha$  show that  $HaBr_5$  in some aspects continues the regularities in properties within the group 5 (stabilization of the pentavalent form, increase in ionization potentials, energies of electronic transitions, crystal-field splitting, covalency) and that the properties of  $NbBr_5$  and  $TaBr_5$  should be more similar than those of  $HaBr_5$ . Besides the nearly equal interatomic distances  $M-Br$  in  $MBr_5$  niobium and tantalum have similar effective charges (and  $Ha$ —much lower) which together with increasing covalency down the group results in the nearly equal volatility of  $NbBr_5$  and  $TaBr_5$ . The low effective charge on  $Ha$  in  $HaBr_5$  and its high covalency indicate that volatility of pure  $HaBr_5$  should be higher than that of the analogs.

Concerning the interpretation of the gas-phase chromatography experiment<sup>7</sup> the present qualitative analysis of the interaction of the adsorbate molecules with the surface can hardly explain the lower volatility of  $HaBr_5$  molecules compared to  $NbBr_5$  and  $TaBr_5$ . This could mean that the probability of formation of other type compounds can not be excluded. These possible cases will be analyzed in the following publications.

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- <sup>1</sup> I. Zvara, Y. T. Chuburkov, V. Z. Belov, G. V. Buklanov, B. B. Zakhvataev, T. S. Zvarova, O. D. Maslov, R. Caletka, and M. R. Shalayevesky, *J. Inorg. Chem.* **32**, 1885 (1970).
- <sup>2</sup> I. Zvara, V. Z. Belov, L. B. Chelnokov, V. P. Domanov, M. Hussonois, Y. S. Korotkin, V. A. Schegolev, and M. R. Shalayevesky, *Inorg. Nucl. Chem. Lett.* **7**, 1109 (1971).
- <sup>3</sup> S. N. Timokhin, K. U. Zin, and V. P. Domanov, in Abstracts of International Conference "Actinides-89" (Tashkent, Russia, 1989), p. 227.
- <sup>4</sup> I. Zvara, in Proceedings of the International School Seminar on Heavy Ion Physics (JINR D7-87-68, Dubna, 1987), p. 145.
- <sup>5</sup> I. Zvara, B. Eichler, V. Z. Belov, T. S. Zvarova, Y. S. Korotkin, M. R. Shalayevesky, V. A. Schegolev, and M. Hussonois, *Radiokhimiya* **16**, 720 (1974) [*Sov. Radiochem.* **16**, 709 (1974)].
- <sup>6</sup> H. W. Gäggeler, D. T. Jost, U. Baltensperger, Y. Nai-Qi, K. E. Gregorich, C. M. Gannett, H. L. Hall, R. A. Henderson, D. M. Lee, J. D. Li, M. J. Nurmia, D. C. Hoffman, A. Türler, Ch. Lienert, M. Schädel, W. Bröchle, J. V. Kratz, H. P. Zimmermann, and U. W. Scherer, Report PSI-Bericht Nr 49, 1989.
- <sup>7</sup> H. W. Gäggeler, D. T. Jost, J. Kovacs, U. W. Scherer, A. Weber, D. Vermeulen, A. Türler, K. E. Gregorich, R. A. Henderson, K. R. Czerwinski, B. Kadkhodayan, D. M. Lee, M. J. Nurmia, D. C. Hoffman, J. V. Kratz, M. K. Göber, H. P. Zimmerman, M. Schädel, W. Bröchle, E. Schimpf, and I. Zvara, Report PSI, PSI-PR-91-32, 1991; *Radiochim. Acta* (to be published).
- <sup>8</sup> (a) A. Türler and H. W. Gäggeler (private communication); (b) D. C. Hoffman, Report LBL-29815, 1990; (c) A. Türler, H. W. Gäggeler, K. E. Gregorich, H. Barth, W. Bröchle, K. R. Czerwinski, M. K. Göber, N. J. Hannik, R. A. Henderson, D. C. Hoffman, D. T. Jost, C. D. Kacher, B. Kadkhodayan, J. Kovacs, J. V. Kratz, S. A. Kreek, D. M. Lee, J. D. Leyba, M. J. Nurmia, M. Schädel, U. W. Scherer, E. Schimpf, D. Vermeulen, A. Weber, H. P. Zimmerman, and I. Zvara, in Proceedings of MARC II Conference (Kona, Hawaii, 1991), to be published in *J. Radioanal. Nucl. Chem.*; Report LBL-31442, 1991.
- <sup>9</sup> B. L. Zhuikov, V. A. Glebov, V. S. Nefedov, and I. Zvara, *Radiochim. Acta* (to be published).
- <sup>10</sup> V. G. Pershina, W.-D. Sepp, B. Fricke, and A. Rosen, *J. Chem. Phys.* **96**, 8367 (1992).
- <sup>11</sup> A. Rosen and D. E. Ellis, *J. Chem. Phys.* **62**, 3039 (1975).
- <sup>12</sup> R. S. Mulliken, *J. Chem. Phys.* **23**, 1833, 1841 (1955).
- <sup>13</sup> D. Brown, in *Comprehensive Inorganic Chemistry*, edited by J. C. Bailar (Pergamon, Oxford, 1973), Vol. 3, pp. 553–622.
- <sup>14</sup> A. V. Demidov, A. A. Ivanov, L. S. Ivashkevich, A. A. Ischenko, V. P. Spiridonov, L. Almlöf, and T. G. Strand, *Chem. Phys. Lett.* **64**, 528 (1979).
- <sup>15</sup> B. Fricke and E. Johnson, *Radiochim. Acta* (to be published).
- <sup>16</sup> Gmelin Handbuch, *Protactinium* (Springer-Verlag, Berlin, Heidelberg, New York, 1977), Vol. 2, pp. 6, 65.
- <sup>17</sup> See AIP document no. PAPS JCPA-97-1116-2 for 2 pages of "Molecular orbitals of  $HaBr_5$ ." Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for each microfiche (60 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
- <sup>18</sup> L. G. Hubert-Pfalzgraf, M. Postel, and J. G. Riess, in *Comprehensive Coordination Chemistry*, edited by G. Wilkinson (Pergamon, Oxford, 1978), Vol. 3, p. 589.
- <sup>19</sup> J. H. Canterford and R. Colton, in *Halides of the Second and Third Row Transition Metals* (Wiley, London, 1968).
- <sup>20</sup> A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1976), p. 308.