

Relativistic pseudopotential calculations for HBr^+ , HBr , HBr^- , HI^+ , HI , and HI^-

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(Received 18 December 1986; accepted 16 March 1987)

Valence SCF/CI calculations using nonrelativistic, relativistic, and semiempirical pseudopotentials have been carried out for the ground states of HBr^i and HI^i ($i = +1, 0, -1$). Autoionization of HBr^- and HI^- is characterized by the crossing points between the Born–Oppenheimer potential energy curves of the negative and neutral molecules. Relativistic and correlation effects are discussed for several molecular properties. Using semiempirical pseudopotentials + valence-CI, our calculated values for HX and HX^+ ($X = \text{Br}, \text{I}$) are in good agreement with experiment. The crossing between the $^1\Sigma^+$ (HX) and $^2\Sigma^+$ (HX^-) curves is calculated to occur at 1.70 Å for HBr/HBr^- and 1.84 Å for HI/HI^- . Dissociative attachment energies for HX/HX^- are compared with results from low-energy electron scattering experiments.

I. INTRODUCTION

Any reasonable treatment of heavy-atom molecules by quantum chemical methods has to take into account relativistic effects on bonding properties. However, relativistic effects in bromine and iodine compounds are rather small within the valence region, so that spin–orbit coupling can be treated perturbatively. On the other hand, all-electron calculations are very expensive in computer time. To handle such systems, spin–orbit averaged relativistic pseudopotentials (ARPP), also called averaged relativistic effective core potentials (AREP)¹ or one-component quasirelativistic pseudopotentials,² seem to be a promising approach. A general description of the calculational method was given in an earlier paper² and will not be repeated here.

In this paper, relativistic and correlation effects are studied for several properties (bond lengths, dissociation energies, force constants, electron affinities, crossing points, and crossing-point energies) by successively using nonrelativistic (NRPP), relativistic (ARPP), and semiempirical or correlated pseudopotentials (SEPP). These pseudopotentials are derived by adjusting the parameters to nonrelativistic, relativistic or experimental ionization energies of the Br^{6+} and I^{6+} ions, as described in detail in Ref. 2. Core-valence correlation is taken into account in the SEPP potentials by a dipole core-polarization potential.^{2–7} Valence correlation is calculated by means of a CI procedure with single and double excitations (CISD). Such a procedure leads to good results for atomic and molecular properties; e.g., the bond distances in HBr , HI , Br_2 , and I_2 differ from the experimental values by less than 0.8%.²

Experimental results for the ground states are available for the neutral and positively charged hydrides of bromine and iodine.⁸ HBr^- , HI^- , and generally the negative halogen–hydride ions are unstable and autoionize into the neu-

tral molecules, as is known from low energy electron–molecule scattering experiments.^{9–14} This can be rationalized by considering the dipole moments of the neutral molecules (HBr : 0.82 D, HI : 0.44 D),⁸ which are lower than the critical value of 1.625 D required for binding an electron calculated in a dipole potential¹⁵ (see also Refs. 16 and 17 for these problems). In addition, the dipole moments of HBr and HI are lower than those of HF (1.82 D) and HCl (1.11 D),⁸ the negative ions of which are also unstable. Within a certain accuracy, the HX/HX^- autoionization crossing points and the corresponding energies can be calculated by using local basis sets without additional plane-wave states; this is not true for transition moments, however.

In the next section, the results are presented for the different levels of the pseudopotential approximation. The final section is devoted to a discussion of the relativistic and correlation effects, and the autoionization process at the CISD level.

II. CALCULATIONS AND RESULTS

All of our present molecular calculations were done with the same pseudopotential parameters and basis sets as for HBr and HI ($9s/6p/2d$ GTO basis set for Br and I and $5s/2p$ GTO basis set for H).² For the nonrelativistic and relativistic pseudopotential SCF calculations, we used a modified version of the program GAUSSIAN82,^{18,19} whereas the CISD calculations with the semiempirical pseudopotential were carried out with the program MELD,²⁰ using the size-consistency correction by Pople *et al.*²¹ The total number of configuration state functions was 16 775 for the HX^- molecules ($X = \text{Br}, \text{I}$). The basis set superposition errors are lower than 0.01 eV in all cases. Results for the neutral molecules have already been presented in Ref. 2.

As shown in our earlier paper,² spin–orbit effects are

small at the equilibrium distance for these molecules. This results from the $p_{3/2}/p_{1/2}$ mixing which leads to the formation of a nearly pure σ bond (see for example, Refs. 22 and 23). Therefore, it is sufficient to consider the spin-orbit splitting of the separated atoms only; expensive calculations with two- or four-component pseudopotentials are not necessary for this type of molecule, and the Λ - S coupling still holds within a certain accuracy. Consequently, the experimental spin-orbit corrections for the HBr^+ and HI^+ ions (the difference between the lowest spin-orbit coupled and the j -averaged state) can be obtained from the Moore tables²⁴ as $\Delta D^{\text{SO}}(\text{HBr}^+) = \Delta E_{\text{SO}}(\text{Br}^+) = -0.183$ eV and $\Delta D^{\text{SO}}(\text{HI}^+) = \Delta E_{\text{SO}}(\text{I}^+) = -0.382$ eV. For comparison, our Dirac-Fock calculations (DF) with the program MCDF/BENA²⁵⁻²⁷ including QED corrections²⁸⁻³⁰ yield $\Delta E_{\text{SO}}(\text{Br}^+) = -0.171$ eV and $\Delta E_{\text{SO}}(\text{I}^+) = -0.381$ eV.

In Table I, the calculated molecular properties are listed for HBr^+ and HI^+ together with the results for HBr and HI . The values are not corrected for size-consistency errors. The spin-orbit corrections to the dissociation energies are accounted for using the ΔE_{SO} values presented above, by incorporating the experimental spin-orbit energies²⁴ for the semiempirical and DF spin-orbit energies²⁵⁻³⁰ for the relativistic pseudopotentials. Because the deviations in equilibrium distances between the neutral² and positively charged halogen hydrides are small (Table I), the vertical ionization energies differ from the adiabatic ones by less than 0.01 eV. Therefore, only the adiabatic values are presented in Table I.

$\text{HX}(^1\Sigma^+)/\text{HX}^-(^2\Sigma^+)$ crossing points r_{cr} ($X = \text{Br}, \text{I}$)

and crossing-point energies $\Delta E_{\text{cr}} = E(r_{\text{cr}}) - E(r_e; \text{HX})$ at the nonrelativistic, relativistic, and semiempirical level are also shown in Table I. As mentioned above, plane waves are not included, but we are using smooth s -, p -, and d -type functions in our calculations (down to 0.01 for the s and 0.024 for the p exponents, e.g.; for details of the basis set see Ref. 2). Consequently, we feel that adding plane waves would not significantly affect the crossing points. At the CISD level, the Born-Oppenheimer ground state energy curves are shown in Fig. 1 for HBr/HBr^- and in Fig. 2 for HI/HI^- . The zero of the energy scale is chosen as the energy of the dissociated atoms H and X ($X = \text{Br}, \text{I}$).

III. DISCUSSION

A detailed discussion of relativistic and correlation effects in HBr and HI is given in Ref. 2. As shown in Table I, the relativistic bond contraction ($r_e^{\text{NR}} - r_e^{\text{R}}$) is less than 0.5% for HBr^+ and HI^+ and therefore negligible; a similar result was found for the neutral molecules. The fact that $r_e(\text{HX}^+) = r_e(\text{HX})$ is verified on all the computational levels considered here. Correlation effects on bond distances are also very small ($< 0.6\%$). Pople's size-consistency correction²¹ affects the results only slightly: $r_e = 1.433$ Å, $D_e = 3.63$ eV (HBr^+); $r_e = 1.620$ Å, $D_e = 2.83$ eV (HI^+). For the dissociation energies we calculate a relativistic decrease of 0.21 eV for HBr^+ and 0.46 eV for HI^+ , including spin-orbit coupling in the approximation described above. In comparison, the effect of correlation ($D_e^{\text{SE}} - D_e^{\text{R}}$), 1.29

TABLE I. Equilibrium distances r_e , dissociation energies D_e , electron affinities EA, and force constants k_e for the $^2\Pi/^1\Sigma^+$ ground states of the molecules HX^+/HX ($X = \text{Br}, \text{I}$). The values are corrected for spin-orbit coupling as described in the text. Crossing points r_{cr} and corresponding energies $\Delta E_{\text{cr}} = E(r_{\text{cr}}) - E(r_e; \text{HX})$ (see Fig. 1) for the Born-Oppenheimer potential curves HX/HX^- ($X = \text{Br}, \text{I}$) are also given. NRPP stands for the nonrelativistic, ARPP for the j -averaged relativistic, and SEPP for the semiempirical (correlated) pseudopotential. Experimental results are from Ref. 8.

			NRPP	ARPP	SEPP	Expt.
r_e	(Å)	HBr^+	1.426	1.424	1.429	1.448
		HBr	1.395	1.393	1.398	1.413
		HI^+	1.629	1.621	1.615	1.62
		HI	1.606	1.597	1.593	1.610
D_e	(eV)	HBr^+	2.97	2.76	3.56	4.05
		HBr	2.92	2.74	3.68	3.92
		HI^+	2.30	1.84	2.76	3.26
		HI	2.37	1.95	3.05	3.20
EA	(eV)	HBr^+	10.83	10.77	11.35	11.67
		HI^+	9.77	9.65	10.32	10.38
k_e	(mdyn/Å)	HBr^+	4.56	4.48	3.78	3.50
		HBr	4.72	4.78	4.40	4.11
		HI^+	3.33	3.19	2.76	2.77
		HI	3.28	3.28	3.63	3.24
r_{cr}	(Å)	HBr/HBr^-	1.741	1.738	1.695	
		HI/HI^-	1.901	1.890	1.838	
ΔE_{cr}	(eV)	HBr/HBr^-	0.662	0.631	0.732	
		HI/HI^-	0.775	0.730	0.422	

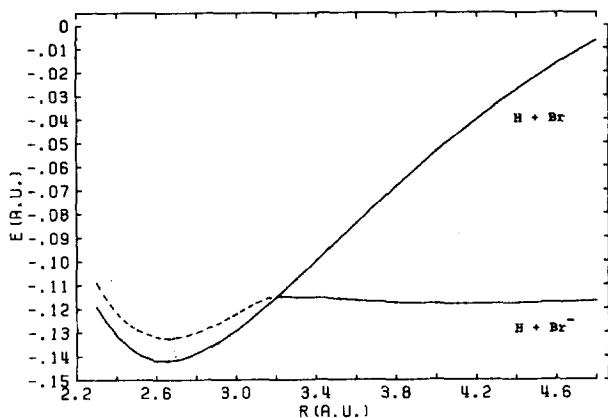


FIG. 1. Calculated potential energy curves for the ground states of HBr and HBr^- .

eV for HBr^+ and 1.42 eV for HI^+ , is much larger. Nevertheless, the total relativistic corrections to the dissociation energies amount to < 14% of the experimental values and are, therefore, nonnegligible. At the CISD level, our results for bond distances, dissociation energies, electron affinities, and force constants are in good agreement with the experimental results,⁸ and the accuracy is about the same as for the values of the neutral molecules.² We now turn to the discussion of the autoionization of the negatively charged molecules.

In Figs. 1 and 2 the HX/HX^- ($X = \text{Br}, \text{I}$) potential curves are presented. Note, that the dashed $^2\Sigma^+$ (HX^-) line in both figures, which runs essentially parallel to the $^1\Sigma^+$ – HX curve, does not describe the real behavior of the potential, because the electron is not bound at distances smaller than the crossing point r_{cr} . This part of the curve is an artifact due to the local basis set used in our work; inclusion of plane waves would transfer the upper potential-curve into the lower one, that of the neutral molecules. The overall behavior of the two potential curves HX/HX^- ($X = \text{Br}, \text{I}$) is very similar to that of the system HCl/HCl^- , calculated by Bettendorff *et al.*³¹ or Goldstein *et al.*³² For $r > r_{\text{cr}}$ a well defined $^2\Sigma^+$ negative ion state exists with a shallow minimum. Near the crossing point a local maximum is found. It occurs at $r_{\text{max}} = 1.708 \text{ \AA}$ for HBr^- and 1.797 \AA for HI^- and

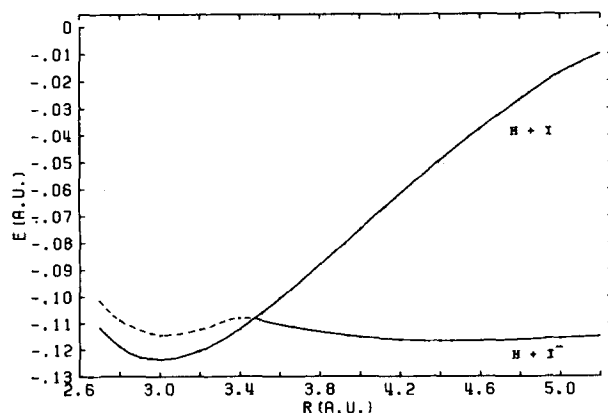


FIG. 2. Calculated potential energy curves for the ground states of HI and HI^- .

has an energy below the dissociation limit in the case for HBr^- . Hence, $\Delta E_d = E(r = \infty; \text{H}, \text{Br}^-) - E(r_e; \text{HBr}) - \frac{1}{2}\omega_e(\text{HBr})$ is the energy difference measured by electron dissociative attachments^{9,10,12} according to the definition of experimentalists. In contrast, the local maximum of the HI^- potential curve is 0.06 eV above the dissociation limit. Using the experimental ω_e ,⁸ the calculated values for the dissociative attachment are $\Delta E_d(\text{HBr}^-) = 0.64 \text{ eV}$ and $\Delta E_d(\text{HI}^-) = 0.28 \text{ eV}$. Because these energies are small, one should correct for spin-orbit coupling before comparing with experimental data. Such effects are negligible for the system $\text{H} + \text{X}^-$ (X^- is a closed-shell ion; $\text{X} = \text{Br}, \text{I}$), therefore, we have to consider only the molecular energetic spin-orbit decrease for the neutral molecules, which is calculated to 0.01 eV for HBr and to 0.06 eV for HI.² In this way, the spin-orbit corrected energies for the dissociative electron attachment are 0.65 eV for HBr and 0.34 eV for HI, according to our calculations. This is not in satisfactory agreement with the experimental result of 0.39 eV by Ziesel *et al.* for the HBr/HBr^- system,¹² which is nearly the same value as the difference between the electron affinity of the Br atom and the dissociation energy of the HBr molecule, $\Delta E_d(\text{HBr}/\text{HBr}^-) = D_e(\text{HBr}) - \text{EA}(\text{Br})$. We expect that a MRCI ansatz with an extension of the basis set would bring our calculated value more to the experimental one. At the CISD level our error in $D_e(\text{HBr})$ is 0.14 eV, that in $\text{EA}(\text{Br})$ 0.47 eV; using $\Delta E_d = D_e - \text{EA}$, this would lead to an error of 0.23 eV for ΔE_{cr} . With this, the corrected E_{cr} value is 0.42 eV and, therefore, in good agreement to the 0.39 eV by Ziesel *et al.* For the dissociative attachment of the HI molecule, only the uncertain results of Frost *et al.*⁹ and Christophorou¹⁰ are available. Their measurements yield a HI/HI^- peak energy appearing $\sim 0.1\text{--}0.3 \text{ eV}$ lower as in HBr/HBr^- , which agrees with our smaller calculated value for HI compared to that for HBr.

As mentioned above, our calculated HBr^- and HI^- potential curves show, at distances $r > r_{\text{cr}}$, a shallow minimum with a depth of 0.09 eV at $r_{\text{min}} = 2.193 \text{ \AA}$ for HBr^- and 0.18 eV at 2.357 \AA for HI^- . From the calculated force constants (0.0079 a.u. for HBr^- and 0.010 a.u. for HI^-) we obtain a zero-point vibrational energy of 0.03 eV in the case of HBr^- and of 0.05 eV for HI^- . Hence, according to our calculations, HX^- ($X = \text{Br}, \text{I}$) may be metastable at $r > r_{\text{cr}}$.

As shown in Table I, relativistic effects decrease the crossing point by less than 0.6%. Against that, the total decrease from correlation is 2.5% for HBr/HBr^- and 2.8% for HI/HI^- . Similarly, relativistic influences in the corresponding crossing-point energies ΔE_{cr} are small and can be neglected within the accuracy of the pseudopotential method.

IV. CONCLUSION

We have used pseudopotentials at various levels of approximations to study relativistic and correlation effects for the ground states of the molecules HX^+ , HX , and HX^- ($X = \text{Br}, \text{I}$). Our results for the HX^+ molecules are in good agreement with experimental data. The HX^- molecule is calculated to be metastable at distances $r > r_{\text{cr}}$. We hope that this result will be confirmed by future measurements.

ACKNOWLEDGMENT

We thank Dr. U. Wedig for implementing and modifying the program MELD.

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