Interaction components in the hydrogen halide dications

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Received 12 December 2006; in final form 22 January 2007
Available online 27 January 2007

Abstract

We have theoretically investigated the interatomic interaction in the low-lying states of HX 2+ dications (X = F, Cl, Br, I) by combining results from semiempirical method with ab initio calculations. Main targets have been the complete characterization of the dependence of the charge transfer on the internuclear distance and on the nature of X atom, together with the assessment of its role with respect to other interaction components. The present analysis accounts for differences in the experimental findings related to the features of the permitted bound levels, which are lacking in HF 2+ and increase in number and stability on going towards HI 2+.

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1. Introduction

The experimental and theoretical characterization of the fundamental properties of multiply charged molecular ions, such as energetics, structure, stability, lifetime and fragmentation patterns, is of great interest to understand and to model the behavior of plasmas, ionosphere and astrophysical environments. Most such features are critically determined by the balance of the attractive and repulsive components of the forces between the atomic or ionic constituents. Therefore, it is of great relevance to perform systematic investigations, combining experimental and theoretical information, to cast light on the nature and interplay of these forces.

Among the dications, the doubly charged hydrogen halides, HX 2+ (X = F, Cl, Br, I), are particularly well suited prototype subjects of study, since they are small diatoms and the H atomic partner cannot exist asymptotically as a dication. This simplifies the description and rationalization of their features. Several experimental studies have been carried out on HX 2+ dications using many techniques [1–14]. In particular, a systematic investigation by a single technique (photo ionization mass spectrometry by synchrotron radiation), allowed the accurate determination of the threshold energies for the formation of molecular dications in metastable and dissociative states [15–17]. From a theoretical point of view, ab initio [1,9,18–28] and semiempirical methods [17,29,30] have been used to predict and explain properties of HX 2+ in connection with experimental determinations [1–17]. In particular, a semiempirical model of the interaction between the atomic fragments in HX 2+ has been introduced by us in order to rationalize the experimental observations. This method leads to a representation of the potential energy of interatomic interaction as a combination of some leading components expressed in a simple and natural analytical form, allowing the simple calculation of dication properties[29,30]. In particular, it underlines the selective role of charge transfer in determining the different degree of stability along the series [17]. However, an extensive and systematic comparison between ab initio results and semiempirical predictions is still lacking. This comparison would be very useful in order to understand the origin of systematic variation in the electronic structure, energetics, lifetime, Franck–Condon factors, energy barriers and spacing of internal quantum states, when going from the lighter to the heavier HX 2+ dications.

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In this work, for HF$^{2+}$, HCl$^{2+}$, and HBr$^{2+}$, we have carried out \textit{ab initio} theoretical calculations in order to perform such a comparison. We have computed accurate potential energy curves for the low-lying dication states between 30 and 44 \textit{eV} and carried out an electron density analysis in order to establish how the charge distribution varies along the series and as a function of the internuclear distance.

Further, the comparison between \textit{ab initio} and semiempirical predictions has allowed us to improve the semiempirical method and use it to define the different role of the leading interaction components, namely charge transfer (CT), electrostatic and induction, in the HX$^{2+}$ series. The selective role of the CT component [17,29,30], associated to the partial mobility of the more external electron within the diatom, is analyzed in detail in Section 3.

2. Theoretical calculations

Both, \textit{ab initio} and semiempirical calculations, have been performed on the HX$^{2+}$ dications. Our semiempirical model has been used for the complete series HF$^{2+}$, HCl$^{2+}$, HBr$^{2+}$, and HI$^{2+}$. We recall here that the method consists in the identification of the nature and consequent modeling of the interatomic potential operating in the two asymptotic configurations of HX$^{2+}$, namely the one corresponding to H and X$^{2+}$ and the other one corresponding to H$^+$ and X$^+$ [17,29,30]. In the first case, the interaction potential is described as a combination of dispersion and induction attractive components and size effect repulsion. For the second case, adiabatically correlating with the low-lying states ($^{3}\Sigma^-, \, ^{1}\Lambda$ and $^{1}\Sigma^+$) of HX$^{2+}$, the interatomic potential depends on an electrostatic contribution, due to the Coulomb repulsion between the two ionic fragments and charge-quadrupole attraction or repulsion, combined with an induction attraction. These two limiting configurations, which give origin to a manifold of states with different symmetry [29,30], are coupled by CT effects. All these interaction components are represented by simple analytical functions, whose parameters are related to basic physical properties of the atomic partners involved [17,29,30].

The \textit{ab initio} potential energy and electronic structure curves for many low-lying electronic states of HF$^{2+}$, HCl$^{2+}$, and HBr$^{2+}$ dications have been obtained by the CASSCF method for 6 electron in 10 orbitals, followed by internally contracted, multi-reference configuration interaction (MRCI) calculations accounting for the single and double excitations of all the CAS configurations, using the program package MOLPRO [31]. The basis set used is the aug-cc-pVQZ basis of Dunning [32,33]. For each molecule, the lowest lying states in each symmetry ($\Sigma^+$, $\Sigma^-$, $\Pi$ and $\Delta$) of singlet and triplet spin, plus the $^5\Sigma^-$ state, have been investigated.

3. Discussion

The low-lying electronic states of the heavier HX$^{2+}$ dications are sufficiently stable to support bound states. The \textit{ab initio} and semiempirical potential energy curves for the low-lying states of HCl$^{2+}$ and HBr$^{2+}$ are shown in Figs. 1 and 2a, respectively. All these states correlate asymptotically with X$^+ + H^+$. The agreement of the semiempirical curves with the \textit{ab initio} ones is very satisfactory, in spite of some discrepancies in few details of the shape. Tables 1 and 2 report the main features of the states, namely the equilibrium distance, the energy at the minimum of the potential well (relative to the neutral ground state at equilibrium) and relevant barriers towards dissociation. As can been seen, the model is able to predict the energies of the states within 0.1 eV of the \textit{ab initio} ones for HCl$^{2+}$, and within 0.2–0.5 eV for HBr$^{2+}$. The dissociation barriers are also predicted by the model with a satisfactory accuracy. While the energies of the vibrational levels predicted by the semiempirical method are, in both systems, consistent with or slightly larger than the experimental results [29,30], those obtained by the \textit{ab initio} calculations appears to be systematically slightly smaller.

Figs. 1 and 2b show a comparison of the predicted behaviors for the dissociative states $^{1,3}\Pi$ and for the weakly bound $^3\Sigma^-$ state, again for the HCl$^{2+}$ and HBr$^{2+}$ systems. The $^3\Sigma^-$ state correlates asymptotically with X$^{2+}$ and the \textit{ab initio} results show a small discrepancy of less than 0.5 eV in reproducing the atomic double ionization energy. This state exhibits a substantial non-covalent nature, since the charge remains at all distances confined on the halogen atom (see the discussion below), confirming the starting assumption of the semiempirical model [29]. In all systems

![Fig. 1. Comparison between \textit{ab initio}, semiempirical and semiempirical corrected potential energy curves for HCl$^{2+}$ in the low-lying metastable states (a) and for dissociative ($^1\Pi$) and weakly bound ($^3\Sigma^-$) states (b). Semiempirical corrected curves, concerning both $\Pi$ states, are practically coincident with \textit{ab initio} curves for internuclear distances larger than 1.5 \text{Å}.](image-url)
investigated both by \textit{ab initio} and by the semiempirical model, the latter predicts for the $^5\Sigma^-/C_0$ state a slightly deeper potential well (see also Ref. [28]). This could partially be due to the fact that the model evaluates better the long range induction attraction.

The dissociative $\Pi$ states, asymptotically correlating with $X^+ + H^+$, are an interesting case where the comparison with the \textit{ab initio} results can be usefully exploited to fine-tune the semiempirical model. As previously discussed [29,30], the shape of these curves depends critically on the strength of the CT component, which was initially set to $1/3$ of the value used for the $^3\Sigma^-$ ground state (curves labeled ‘Semiempirical’ in Figs. 1 and 2) [17,29,30]. The figures show that the assigned amount of charge transfer appears to be slightly smaller than it should be, leading to a too steep repulsive potential when compared to the \textit{ab initio} curves at intermediate and short range. By adjusting this single CT scaling coefficient, one can achieve an almost perfect match in the Franck–Condon range (curves labeled ‘Semiempirical corrected’ in Figs. 1 and 2). The improved values for the CT coefficient are 0.34 and 0.50 for the $^3\Pi$ and $^1\Pi$ states of HCl$^2+$, respectively, and 0.45 and 0.60 for the same states of HBr$^2+$.

The semiempirical model thus demonstrates that the different behavior of HX$^2+$ dications can be mainly ascribed to the different role of CT effects. To further investigate this aspect, we have computed the atomic Mulliken charges of the various MRCI states, correlating either with $X^+$ or $X^2+$, as a function of the internuclear distance. Fig. 3 reports the partial charge on the halogen atom for dications in the ground state $^3\Sigma^-$ and shows that, in general, the calculated electron transfer from $X^+$ to $H^+$ increases as the two ions approach. This transfer of charge is very weak for HF$^2+$, whose potential remains in fact repulsive at all distances, but is much larger in the case of HCl$^2+$ and HBr$^2+$. Here the partial charge around the equilibrium distance (shaded region in Fig. 3) assumes values significantly larger than +1. The effect of such a transfer of charge is interpreted, in our model, as arising from the coupling of the low-lying states, asymptotically correlating with $X^+ + H^+$, with excited states of the same symmetry, leading asymptotically to $X^2+ + H$ [29,30]. The semiempirical method explains the differences in the results for the various molecules in terms of a variation in the energy gap between the coupled states, which is maximum for

![Figure 2](image-url)
HF$^{2+}$ and minimum for HI$^{2+}$ [17]. Similar results are obtained for the other low-lying states, $^1\Sigma$ and $^1\Pi$, while in the $^1\Pi$ states, also asymptotically correlating with $X^++H^+$, the calculated partial charge assumes values slightly lower. As an example, HCl$^{2+}$ shows around the equilibrium distance of the metastable states (≈1.5 Å) a charge decreasing from 1.33 to 1.23, in agreement with the reduced role of the CT component (see Fig. 4). For all the systems in the $^3\Sigma^-$ state, the double positive charge remains essentially confined on the halogen atom at all distances, confirming that the involved interaction is mainly non-covalent (i.e. induction and dispersion attraction combined with size repulsion) [29,30].

The reliability of our semiempirical model enables us to carry out a more detailed analysis of the complete HX$^{2+}$ dication series and to examine the various interaction components as a function of the internuclear distance. This provides information, not only on the CT component, which plays a crucial role at intermediate and short distances, but also on the components dominant at long range. Such components are the electrostatic interaction and the effect arising from induction dumped by the penetration of $H^+$ into the outer electronic shell of $X^+$ [29]. The results for the dications in their ground state $^3\Sigma^-$ are reported in Fig. 5, where the shaded zone indicates the equilibrium distance region (since HF$^{2+}$ does not exhibit bound states, the distance of interest is that of the inflection point) [17]. A comparison between the curves for the various systems in the bond distance region suggests immediately that the electrostatic component (repulsive) dominates with respect to the induction and CT components (attractive) for HF$^{2+}$, while for the heavier systems the latter play a more effective role, also considering that the equilibrium distance increases along the series. The enhanced role of induction along the series, in addition to the CT effect discussed above, is related to the increase in $X^+$ polarizability.

4. Conclusion

This Letter can be considered as the conclusion of some experimental and theoretical efforts done in our laboratory [12,15–17,29,30] in order to understand, not only the dynamics of the double photo ionization of hydrogen halides, but also the nature of the bond in the product HX$^{2+}$ dications and in order to model the interaction between the two atomic partners. In the present Letter we have compared the results obtained by a semiempirical model with ab initio calculations: we have analyzed in a direct way many dicationic potential energy curves and some specific properties like the charge transfer. It is here definitively demonstrated that the latter, considered a fundamental process in our semiempirical model, selectively affects the features of the HX$^{2+}$ homologous series.

The present investigation help us in understanding, on a quantitative basis, the fact that the metastable states of HX$^{2+}$ support a number of bound states increasing when
going from HF$^{2+}$, which is only dissociative, towards HI$^{2+}$ which has many and more stable states.

The obtained results allow us to also to rationalize the fact that the dissociative channel leading to H$^+$ + X$^+$ becomes less important moving towards the heavier diatoms, since the barrier against the coulombic explosion increases in height and width.

Acknowledgements

This work is partially supported by the Italian MUR (Ministero dell’Università e della Ricerca) through PRIN and FIRB projects.

References