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Electronic States of the Xe_nHCl Systems in Gas and Condensed Phases

by

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ELECTRONIC STATES OF THE $Xe_n HCl$ SYSTEMS IN GAS AND CONDENSED PHASES

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Abstract

Systems formed by one Cl, one H and one or several Xe atoms are considered by the semiempirical diatomics-in-ionic-systems method, which takes into account the charge delocalization in ionic states and the coupling between the neutral and ionic states. Calculations are performed both for gas-phase systems, such as van der Waals complexes and clusters $Xe_n HCl$ (n = 1,2,4,8,12) and ionic molecules $(HXe_n)^+ Cl^-$, and for systems formed in Xe solids doped by HCl molecules. The calculations give the structure of the systems, dissociation energies and energies of electronic transitions. The calculations show, in particular, the existence of the ground-state ionic molecule $(HXe)^+ Cl^-$, the decrease of the HCl electronic excitation energy in clusters and solids, and the increase of the emission photon energy of the ionic $HXe_n^+ Cl^-$ systems as compared to the $Xe_n^+ Cl^-$ molecule.

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1. Introduction

Systems formed by rare-gas atoms R and halogen atoms X or halogen-containing molecules have recently attracted much attention, particularly in regard to their spectroscopic properties. Save for some spatial cases, the halogen molecules X_2 and hydrogen halides HX form with rare-gas atoms van der Waals complexes, whose vibrational and rotational spectroscopy has been intensively studied.[1-9] The infrared spectroscopy of the molecules X_2 and HCl has been studied also in rare-gas matrixes.[10,11] Both in the van der Waals complexes and in the rare-gas matrixes the electronic structure of the molecules X_2 and HX is unaffected by the rare-gas atoms, which can thus be considered as real inert atoms. Even in excited valence states, the molecules are not affected significantly by the rare-gas atoms either in the gas phase[12] or in solids.[13,14]

The rather different class of rare-gas-halogen systems contain quasistable ionic molecules like R^+X^- or $R_n^+X^-$ (n > 1) with electron transfer from the rare-gas atom (or atoms) to the halogen atom.[15-17] In these molecules the halogen and rare-gas atoms form a common electronic structure, in contrast to the van der Waals complexes and halogen molecules in a matrix. The ionic rare-gas-halogen molecules have also been detected in the condensed phase.[18-22] Electronic transitions in the ionic rare-gas-halogen molecules are of great interest, especially because of their lasing properties. The neutral R_nX and the ionic $R_n^+X^-$ electronic configurations are coupled one with another. Due to this coupling, the ground-state R_nX systems can not be considered as pure van der Waals complexes, since the coupling contributes to some valence attraction between the halogen and rare-gas atoms.[23] For example, the contribution of the coupling (valence) energy constitute 45% of the XeCl dissociation energy, and the Xe-Cl equilibrium distance (3.23 Å) is much smaller than the sum of the van

der Waals radii of Xe and Cl atoms (4 Å).[24] The coupling between the neutral and ionic configurations becomes much more important in the case of heavy rare-gas atoms Xe and Kr and light halogen atom F, leading, for example, to the formation of XeF_2 or XeF_4 molecules where F atoms can be considered as ligands.[25] Such molecules have also been detected in rare-gas solids.[26] There are even claims about the detection of a $XeCl_2$ molecule in rare-gas solids, although, according to Ref. 20, the Cl_2 molecules preserve their individuality in a rare gas matrix. Excluding F_2 molecules which can be easily dissociated, other halogen molecules, as well as halogen hydrogens, are not much affected by rare gas atoms, as mentioned above.

Theoretical consideration of the electronic structure of the rare-gas-halogen systems R_nX, R_nHX and R_nX_2 in their ground and excited states, including the states with electron transfer, is of obvious interest. _Ab initio_ calculations have been performed for a few systems only, such as RX,[23] ArF, KrF,[27] and with some simplifications, XeF[27] and XeCl.[28] Semiempirical DIM calculations have been performed for a few R_2X systems, however, without taking into account the coupling between neutral and ionic states.[29,30] Some RX potential curves have been constructed using empirical data.[16,31]

In order to calculate the electronic structure of rare-gas-halogen systems with arbitrary numbers of rare-gas atoms, we presented earlier a semiempirical diatomics-in-ionic systems (DIIS) method which takes into account the coupling between electronic configurations with different number of electrons on atoms.[24] The version of the DIIS method presented in Ref. 24 was designed to treat R_nX systems containing one halogen only, and the calculations were performed for different Xe_nCl systems in the gas phase. The DIIS method was applied later to the Xe_nCl systems formed in a Xe solid matrix.[32] In the present paper, we shall extend the DIIS method to the R_nHX systems containing

one halogen atom, one hydrogen atom and an arbitrary number of rare-gas atoms. This version of the DIIS method will be applied to the specific case of the Xe_nHCl systems in gas and condensed phases. The brief description of the DIIS method and its version for the R_nHX systems is given in Sec. 2. Sections 3 and 4 present the results of the calculation of the Xe_2HCl system in different electronic states in the gas phase and Xe solids, respectively. Conclusions are given in Section 5.

2. DIIS Method for R_nHX Systems

The semiempirical DIIS method is presented in Ref. 24 where it was applied for the calculations of the R_nX systems. In this method, the wave function is given as a linear combination of polyatomic wave functions which describe diabatic states with fixed electronic configurations on each atom. In the case of the R_nXH system, the wave function is

$$\Phi = \sum_{i=1}^{J} \sum_{m=1}^{M_i} C_{im} \Phi_{im} \, , \tag{1}$$

where $J = n + 2$ is the number of atoms in the system, Φ_{im} ($i = 1,2...n$) is a polyatomic wave function of the ionic configuration $R_1...R_{i-1}R_{i,m}^+R_{i+1}...R_nX^-H$, with rare-gas $R_{i,m}^+$ ion in the m-orientation of its P-symmetry electronic shell ($M_i = 3$), $\Phi_{n+1,m}$ is a polyatomic wave function of the neutral configuration $R_1...R_nXH$ with the halogen atom X in the m-orientation of its P-symmetry electronic shell ($M_{n+1} = 3$), and $\Phi_{j,1}$ ($M_J = 1$) is a polyatomic wave function of the ionic configuration $R_1...R_nX^-H^+$ with S-symmetry electronic shells of all atoms. The expression (1) does not include the spin-orbit coupling directly,

although the shift of the levels due to the spin-orbit coupling can be accounted for indirectly by the proper incorporation of the diatomic potentials. Representing the wave function as the linear combination (1), we describe the electronic structure by the motion of a positive-charged hole in the system R_nCl^-H with S-symmetry atomic shells. The positive hole changes the symmetry of the atoms except for the hydrogen atom. The 3J-2 diabatic wave functions Φ_{im} produce the (3J-2)×(3J-2) Hamiltonian matrix which determines the eigenstates and eigenvalues of the adiabatic wave function (1).

The DIIS matrix elements are expressed in terms of diatomic fragments of the system.[24] As the polarization energy can not be expressed in a pairwise way, it is singled out into a separate term ϵ_i. The diagonal matrix elements are expressed as a sum of polarization energy ϵ and diatomic diabatic (Coulombic) potentials $\tilde{U}$ with no polarization terms,

$$H_{im,im} = E_i^* + \sum_j E_j + \sum_{j_1} \sum_{j_2(>j_1)} \tilde{U}_{j_1,j_2} + \sum_j \tilde{U}_{j,im} + \epsilon_i \ , \qquad (2)$$

$$j,j_1,j_2 \neq i$$

where E_j is the energy of an atom without a hole (R, X^-, H), E_i^* is the energy of an atom with a hole (R^+, X, H^+), ϵ_i is the polarization energy of neutral atoms in the field of charged atoms ($\epsilon_i = 0$ for the neutral configuration i = n + 1), $\tilde{U}_{j_1,j_2}$ are the Coulombic potentials between pairs of atoms without a hole (R-R, R-X^-, R-H, X^--H), and $\tilde{U}_{j,im}$ are the Coulombic potentials between atoms with a hole and atoms without a hole (R^+-R, R^+-X^-, R^+-H, X-R, X-H, H^+-R, H^+-X). The diatomic polarization terms are excluded from the Coulombic potentials U of the interaction between ions (j) and neutral atoms (j'),[33]

$$\tilde{U}_{jj'} = U_{jj'} - \left[-e^2 \alpha_{j'}/2R_{jj'}^4 \right] \quad . \tag{3}$$

where $\alpha_{j'}$ is the polarizability of the j' atom, and $R_{jj'}$ is the ion-atom separation. In the case of the interaction between two ions or neutral atoms, $\tilde{U}_{jj'} = U_{jj'}$. By using a proper transformation of the orientation of P-functions, it is possible to express $\tilde{U}_{j,im}$ in Eq. (2) in terms of the Coulombic potentials $\tilde{U}$ of Σ- and Π-symmetry. The off-diagonal matrix elements $H_{i_1 m_1, i_2 m_2}$ ($i_2 \neq i_1$) are expressed by the exchange terms $V_{i_1 i_2}$ of the diatomic fragments $i_1 i_2$.[24] The diatomic Coulombic potentials $\tilde{U}$ for the diatomic fragments XeXe, Xe^+Xe, XeCl, Xe^+Cl^- and $XeCl^-$ and the exchange terms between configurations (Xe^+Xe)-$(XeXe^+)$ and $(XeCl)$-(Xe^+Cl^-) are presented in Ref. 24. In the case of the Xe_nClH system, one needs also the Coulombic potentials for the fragments XeH, Xe^+H, XeH^+, ClH, Cl^-H^+ and the exchange terms between the configurations (Xe^+H)-(XeH^+) and (ClH)-(Cl^-H^+).

A. **XeH Diatomic Fragment**

The empirical van der Waals potential of the Xe-H interaction is taken from Ref. 34:

$$U_{XeH}(R) = 0.0274[(3.5/R)^{12} - (3.5/R)^6] \quad . \tag{4}$$

The $(HXe)^+$ Σ-potentials are obtained by fitting the results of an ab initio calculation.[35] In this calculation, the equilibrium distance is $R_e = 1.61$ Å, which coincides with the spectroscopic value of 1.60 Å.[36] The ab initio dissociation energy is $D_e = 4.05$ eV ($D_o = 3.90$ eV), which is also in good agreement with the empirical value of $D_o = 3.64$ eV obtained by measuring the

proton affinity.[37] In the approximation accepted here, the ground-state (XeH)$^-$ energy is obtained as the eigenvalue of the 2×2 matrix whose elements are

$$H_{11} = U_{\Sigma, XeH^+}, \quad H_{22} = U_{\Sigma, XeH^+}, \quad H_{12} = V_\Sigma \quad , \tag{5}$$

where U_{Σ, Xe^+H} and U_{Σ, XeH^+} are the Coulombic potentials of the diabatic states with $Xe^+ + H$ and $Xe + H^+$ asymptotic configurations, respectively, and V_Σ is the $(Xe^+H)-(XeH^+)$ exchange integral. The potentials U_{Σ, Xe^+H} and U_{Σ, XeH^+} and the exchange integral V_Σ which fit the $\underline{ab}$ $\underline{initio}$[35] ground-state potential 1Σ and the dipole moment μ are expressed in a following way (U, V in eV, R in Å):

$$U_{\Sigma, Xe^+H} = 307\exp(-2.6R) - 4.8/R^4 \tag{6}$$

$$U_{\Sigma, XeH^+} = 1.47 + 5340\exp(-3.2R) - 29.14/R^4 \tag{7}$$

$$V_\Sigma = -414\exp(-2.02R) \tag{8}$$

The Π-potential with the Xe^++H asymptotic configuration is obtained by fitting the $\underline{ab}$ $\underline{initio}$ $^3\Pi$-potential of Ref. 38:

$$U_{\Pi, Xe^+H} = 1710\exp(-3.6R) - 4.8/R^4 \quad . \tag{9}$$

The last terms in Eqs. (6), (7) and (9) representing the polarization energy are excluded when the potentials $\bar{U}$ of Eq. (3) are calculated.

3. HCl Diatomic Fragment

The HCl diatomic fragment contributes the following Coulombic potentials: $U_{\Sigma,ClH}$, U_{Σ,Cl^-H^+}, $U_{\Pi,ClH}$, U_{Σ,Cl^-H}. The electronic configurations Σ_{ClH} and Σ_{ClH}^+ are coupled to each other by an exchange integral $V_{\Sigma,ClH}$, forming a 2×2 matrix whose eigenvalues $1\Sigma_{ClH}$ and $2\Sigma_{ClH}$ represent the potentials of the HCl ground and excited (ionic) states, respectively. The electronic configurations Π_{ClH} and Σ_{Cl^-H} are uncoupled, and therefore the Coulombic potentials $U_{\Pi,ClH}$ and U_{Σ,Cl^-H} coincide with the respective adiabatic potentials Π_{ClH} and Σ_{Cl^-H}.

In the case of the ClH fragment, in contrast to the case of the $(XeH)^+$ fragment, we express analytically not the Coulombic potentials but the adiabatic potentials. The ground state $1\Sigma_{ClH}$ is presented here as a Morse potential which fits the empirical HCl constants, namely $R_e = 1.275$ Å, $\hbar\omega_e = 0.3708$ eV, $D_o = 4.43$ eV ($D_e = 4.615$ eV):

$$1\Sigma_{ClH} = 4.615 G(G-2) \quad , \tag{10}$$

$$G = \exp[-1.87(R-1.275)] \quad . \tag{11}$$

The lowest excited Σ-symmetry adiabatic potential 2Σ is expressed as[39]

$$2\Sigma_{ClH} = 9.985 + 3.6\cdot10^6\exp(-9R) + 303\exp(-2R) - 14.4/R - 55/R^4 \quad , \tag{12}$$

where 9.985 is the difference between $I_H = 13.599$ eV and $A_{Cl} = 3.614$ eV. The potential fits approximately the spectroscopic parameters of the 2Σ state, such as $R_e = 2.51$Å (2.30Å), $\hbar\omega_e = 0.1087$ eV (0.094 eV) and T_o 9.6 eV (9.7 eV),[40] where the numbers in the brackets stand for the potential (12) values. The potential (12) has a second minimum at R = 1.4Å, as in the _ab initio_

calculation of Ref. 39. The exchange integral of the (ClH)-(Cl$^-$H$^+$) coupling

fits the empirical dipole moment $\mu_e = 1.09$D and its derivative 0.94D/Å at the

ground-state equilibrium point,[41]

$$V_{\Sigma,HCl} = -9.25\exp(0.7R) \quad . \tag{13}$$

The adiabatic potentials (10) and (12) are eigenvalues of a 2×2 matrix

similar to that presented by Eq. (5). The off-diagonal elements, $V_{\Sigma,HCl}$, are

given by Eq. (13), whereas the diagonal elements are the diabatic potentials U

which can be expressed in terms of the adiabatic potentials and the exchange

integral:

$$W = (2\Sigma_{ClH} - 1\Sigma_{ClH})^2 - 4(V_{\Sigma,HCl})^2 \tag{14}$$

$$U_{\Sigma,HCl} = \frac{1}{2}(1\Sigma_{ClH} + 2\Sigma_{ClH} - \sqrt{W}) \tag{15}$$

$$U_{\Sigma,H^+Cl^-} = \frac{1}{2}(1\Sigma_{ClH} + 2\Sigma_{ClH} + \sqrt{W}) \quad . \tag{15'}$$

The HCl $^1\Pi$-potential is determined by fitting the ab initio slope of the

potential at the ground-state equilibrium point $R_e = 1.275$ Å and the empirical

transition energy $T_e = 8.12$ eV,[40]

$$U_{\Pi,ClH} = {}^1\Pi_{ClH} = 97.8\exp(-2.57R) \quad . \tag{16}$$

The HCl$^-$ $1{}^2\Sigma$ potential is obtained through ab initio calculations.[42-45]

Reference 42 gives a weakly-repulsive potential curve, whereas in two other

calculations a potential well is found. In the last and most sophisticated

calculation,[44] the potential well is found to be shallow with the location of the minimum at R = 2.1 Å and the energy of dissociation to separated H + Cl$^-$ as D_e = 0.08 eV. A deeper well of D_e = 0.35 eV at the same separation, approximately, is found in Ref. 42. An inspection of experimental data leads us to suggest that at the HCl equilibrium point R_e = 1.275 Å, the HCl$^-$ potential is not higher than the asymptotic H + Cl$^-$ energy.[45] Taking into account this suggestion as well as the results of the ab initio calculations, we construct a HCl$^-$ potential curve with a shallow well of 0.18 eV at 1.5 Å and an energy of -0.1 eV at the HCl equilibrium point R_e = 1.275 Å:

$$U_{Cl^-H} = 1800\exp(-6R) + 12.8\exp(-2.1R) - 4.8/R^4 \quad . \tag{17}$$

3. Xe$_n$HCl van der Waals Complexes and Excited Ionic Molecules

A. XeHCl

The ground-state RHCl systems are typical van der Waals complexes whose vibrational and rotational spectra have been extensively studied.[3-9] The theoretical analysis of these spectra allows us to construct empirical potentials and to determine the equilibrium configurations of the RHCl systems.[46-52] The results concerning the equilibrium configurations of the ArHCl complex, which is most often studied, are rather contradictory. According to some of the calculations, there are two local minima in the collinear ArHCl and ArClH configurations.[46,47] The experimental studies support the presence of two local minima.[8,49,52] However, the acccuracy of the potential energy calculations based on the fitting of experimental data is too low to decide whether the configurations are really collinear.[46] A recent study of ArHCl, as well as KrHCl and XeHCl, gives a bent geometry for the only equilibrium configuration.[51] The XeHCl van der Waals complex has, according to

Ref. 51, a Xe-Cl-H angle of 34° and interatomic distances of $R_{XeCl} = 4.272$ Å and $R_{XeH} = 3.30$ Å. The dissociation energy is found to be $D_o = 0.0255$ eV, which gives for the minimum energy configuration a value $D_e = 0.027$ eV.

According to the results of our semiempirical calculation of the XeHCl van der Waals complex, there are two equilibrium configurations with practically the same minimum energy values. The parameters of these complexes are presented in Table 1, denoted as 1n and 2n, and their geometry is shown in Fig. 1a. One of these configurations has a bent geometry, as in Ref. 51. However, this geometry is close to the perpendicular one with an Xe-Cl-H angle of 78°. The interatomic distances of this configuration are found to be equal to $R_{XeCl} = 4.10$ Å and $R_{XeH} = 4.03$ Å and the dissociation energy equal to $D_e = 0.019$ eV. The second equilibrium configuration has a collinear XeClH geometry with $R_{XeCl} = 3.82$ Å and $D_e = 0.018$ eV. The presence of two equilibrium geometries in the XeHCl van der Waals complex is supported by a similar finding in the case of the ArHCl complex.[8,46,47,49] It is important to note that the location of the equilibrium points is sensitive to very small variations of energy, and consequently the accuracy of the parameters of the van der Waals complex is low. The HCl excitation energies in the van der Waals complex (Table 2) are almost the same as in a free HCl molecule, where they are equal to 8.31 eV and 9.89 eV for the $\Sigma_{HCl} \rightarrow \Pi_{HCl}$ and $\Sigma_{HCl} \rightarrow \Sigma_{H^+Cl^-}$ transitions, respectively. The excitation energy to the states with Xe$\rightarrow$Cl electron transfer (9.3-9.4 eV) is much lower than the energy of electron transfer between the separated Xe atom and HCl molecule, which is equal for our HCl$^-$ potential to 13.05 eV. In the lowest excited states, $k = 2,3$, there are also van der Waals complexes, although with weak bounding between all three atoms. The $k = 2,3$ complexes are not presented in Table 1.

Strongly-bound triatomic ionic molecules are found in all states save for the highest one, k = 7 (Table 1). Even in the ground state, an ionic molecule is formed (1i). The ground-state ionic molecule has a collinear $(HXe)^+Cl^-$ configuration of Σ symmetry and is separated from the van der Waals complex by a barrier of 0.41 eV (Fig. 1b). The energy of this molecule is low, -0.39 eV, as the atoms are linked by two strong bonds, namely $(H-Xe)^+$ and Xe^+-Cl^-, and by Coulombic attraction between a partly-ionized H atom and Cl^- ion. The $(HXe)^+Cl^-$ molecule may be detected because of its large dipole moment of 15 D, although it is not clear which process will lead to the formation of this molecule.

An ionic collinear molecule of Σ symmetry is also formed in the first excited (k = 2) state (2i). The arrangement of the atoms is different from that of the gound-state ionic molecule, namely $(XeH)^+Cl^-$. The ionic molecule is separated from the van der Waals complex of the excited k = 2 state by a barrier of 0.18 eV. The $(XeH)^+Cl^-$ molecule emits in the near UV (λ = 0.232 μm).

In the states k = 4-6 there are four quasistable ionic molecules (Table 1). Three of these molecules (4i-6i) have the structure of a complex formed by an ionic molecule Xe^+Cl^- and a neutral or almost-neutral H-atom bound to the Xe^+Cl^- molecule by polarization forces. The ionic 4i molecule is shown in Fig. 1b. The energy of the H atom separation lies within the limits 0.12-0.18 eV, much larger than in the van der Waals complexes but much less than in the valence-bound molecules. The transition energy to the ground state lies within the limits 7.3-7.5 eV, which well exceeds the transition energy of the $2\Sigma(B)$ and $2\Sigma(C)$ Xe^+Cl^- molecules equal to 4 eV, roughly. The increase in the transition energy as compared to the diatomic case is due to the difference in the ground-state energies of XeClH and XeCl in the configurations of their

respective ionic molecules. In the triatomic case the ground state Cl-H interaction is relatively strong and significantly lowers the XeClH energy.

In the ionic molecule 3i (k = 4), in contrast to the ionic molecules 4i-6i, the H atom shares an important part of the positive charge, which makes the molecule more stable due to the $(Xe-H)^+$ binding (Fig. 1b). Consequently, the energy of the H atom separation is large, 1.26 eV. The transition energy to the ground state is very low, only 0.8 eV.

The foregoing consideration demonstrates that the quasistable ionic XeHCl molecules provides emission both in the near-infrared (3i molecule) and UV regions (2i, 4i-6i molecules). It is important to note that the UV emission of the 4i-6i molecules is of much shorter wavelength than that of the Xe^+Cl^- molecule. Some of these quasistable molecules can be formed by photoexcitation of the XeHCl van der Waals complexes. However, the energy of excitation is high, so that one needs the UV excitation in the case of single-photon excitation. The ionic XeHCl molecules can be formed, probably, by discharge in a Xe-HCl mixture.

B. Xe_2HCl

The XeHCl van der Waals complexes attract more Xe atoms, forming Xe_nHCl clusters. The van der Waals cluster Xe_2HCl is found to have an off-planar geometry with symmetrical arrangement of the two Xe atoms. The interatomic distances are: R_{XeCl} = 4.1 Å, R_{XeH} = 4.05 Å, R_{XeXe} = 4.5 Å. The cluster is rather stable, as the energy for the separation of one Xe atom is as large as 0.043 eV, much larger than the dissociation energy of the XeHCl van der Waals complex. The dissociation energy of the cluster, i.e., the detachment of both Xe atoms, is 0.062 eV (0.031 eV per Xe atom). The excitation energies of the Xe_2HCl cluster are close to those of the XeHCl complex.

A strongly-bound ionic molecule $Cl^-(Xe_2H)^+$ is found in the state $k = 4$ (Fig. 2). The molecule has a plane geometry with symmetrical arrangement of the two Xe atoms. The interatomic distances are: $R_{XeCl} = 3.22$ Å, $R_{XeXe} = 3.6$ Å, $R_{XeH} = 2.61$ Å, $R_{ClH} = 4.56$ Å. The ion Cl^- with a charge $q_{Cl} = 0.93$ is bound to the partly-ionized Xe atoms ($q_{Xe} = +0.34$), like in the $Xe_2^+Cl^-$ molecule. The H atom carries a charge of $q_H = +0.24$ and is bound to the Cl ion by Coulombic attraction. The energy of dissociation to $H + Xe_2^+Cl^-$ is $D_e = 0.33$ eV. The dipole moment of the molecule is as large as 14 D. The energy of transition to the ground state is $T_{4 \to 1} = 1.18$ eV, with a transition moment of about 2 D.

The Xe_2ClH system forms a few other ionic molecules which have the structure of the $Xe_2^+Cl^-H$ molecule with a weakly-bound H atom which is neutral or slightly charged. As in the case of the Xe^+Cl^-H ionic molecules 4i-6i with a weakly-bound H atom, the transition energies to the ground state are much larger than without the H atom, due to the much weaker H-Cl interaction in the ionic $Xe_2^+Cl^-H$ molecule than in the ground-state Xe_2ClH system of the same geometry. A $Xe_2^+Cl^-H$ ionic molecule in the state $k = 4$ is presented in Fig. 2. The energy of dissociation of this molecule to $Xe_2^+Cl^- + H$ is $D_e = 0.09$ eV.

C. $\underline{Xe_4HCl, Xe_8HCl, Xe_{12}HCl}$

The Xe_4HCl, Xe_8HCl and $Xe_{12}HCl$ clusters are considered in the ground state only (Table 2). All of these clusters are of C_4 symmetry with the symmetry axis along the HCl molecule. In the Xe_4HCl cluster, the ClXe lines form an angle of $\theta = 128°$ with the HCl line. The distances are $R_{ClXe} = 3.99$ Å and $R_{HXe} = 4.88$ Å. The dissociation energy of the cluster is 0.172 eV (0.043 eV per Xe atom). In the Xe_8HCl cluster, four of the eight Xe atoms have the same location as in the Xe_4HCl cluster. The location of the other four Xe atoms is: $\theta = 74°$, $R_{ClXe} = 3.96$ Å, $R_{HXe} = 3.81$ Å. The dissociation energy of the Xe_8HCl

cluster is 0.496 eV (0.062 eV per Xe atom). As in the case of the Xe_4HCl

cluster, the addition of four more Xe atoms to the Xe_8HCl cluster does not

change the arrangement of the previous Xe atoms. However, the four new atoms

are located in the $Xe_{12}HCl$ cluster at $R_{ClXe} = 5.5$ Å, much farther from the Cl

atom than the other Xe atoms. The angle is $\theta = 34°$ and the H-Xe distance is

$R_{HXe} = 4.51$ Å. The dissociation energy of the $Xe_{12}HCl$ cluster is 0.851 eV

(0.071 eV per Xe atom).

The dissociation energy per Xe atom in the Xe_nHCl clusters increases with

n up to a maximum value of 0.071 eV for n = 12. The binding in the Xe_nHCl

clusters is of van der Waals origin with a small polarization component

produced by a HCl dipole moment. The number of Xe-Xe interactions in Xe_nHCl

clusters increases faster than n, which explains the increase of the

dissociation energy per one atom. The situation is quite different for Xe_nCl

clusters, where the Xe-Cl interaction is partly of valence origin.[24] For Xe_nCl

clusters, one or two of the Xe atoms are bound much more strongly to the Cl

atom than other Xe atoms, which complicates the dependence of the dissociation

energy on n compared to that of the van der Waals cluster.

The $\Sigma \rightarrow \Pi$ transition energy of the HCl molecule in the clusters decreases

slightly with n down to T = 8 eV for n = 8,12, compared to T = 8.31 eV in a

free HCl. The energy of transition to the k = 4 ionic state depends much more

strongly on the number of Xe atoms. It is equal to T = 8.5 eV for n = 12,

compared to T = 9.3 eV in a van der Waals complex, and T = 13 eV for separated

Xe and HCl. The transition energies of clusters are represented in Table 2.

4. <u>HCl Molecule in a Xe Solid Matrix</u>

We consider here a HCl molecule located at a substitutional site in a Xe

solid matrix. The surrounding twelve Xe atoms form a cage and are considered

together with the H and Cl atoms as a $Xe_{12}HCl$ molecule. All other Xe atoms of the solid form a rigid matrix. THe $Xe_{12}HCl$ molecule is considered here by the DIIS method, which takes into account the electron (hole) delocalization among all 14 atoms of the $Xe_{12}HCl$ molecule but neglects the exchange interaction and electron transfer between the atoms of $Xe_{12}HCl$ and the Xe atoms of the rigid matrix. Any other interactions between the $Xe_{12}HCl$ atoms and the matrix atoms, like van der Waals and polarization interactions, are taken into account in the calculation.[32]

A. Ground State

According to the results of the calculation performed for the ground (k = 1) state, the HCl molecule in the Xe matrix has a fixed location, in contrast to the case of a Cl atom which has some freedom of motion inside the Xe cage.[32] In the equilibrium position, the Cl atom of the HCl molecule is shifted from the cage center at 0.46 Å toward four Xe atoms, forming a symmetric tetragonal $ClXe_4$ pyramid. The HCl molecule is oriented along the pyramidal axis with the H atom located out of the pyramid. The cage is slightly shrunk as compared to the atomic positions of the indeformed matrix, with a distance between neighboring Xe atoms of 4.4 Å. In the presence of the HCl molecule, eight of the cage Xe atoms, including those of the $ClXe_4$ pyramid, are shifted toward the cage center at 0.04 Å and are located at 4.36 Å from the cage center. The interatomic distances in the pyramid are R_{XeXe} = 4.36 Å and R_{ClXe} = 4.05 Å. The distance between the four Xe atoms of the pyramid and the H atom is R_{HXe} = 4.97 Å. Four of the cage atoms located in the plane perpendicular to the HCl molecule are shifted toward the cage center at 0.07 Å and are located at 4.33 Å from the cage center. The ground-state electronic structure is practically unaffected by Xe atoms, as in the case of Xe_nHCl van der Waals complexes or

clusters, and the interatomic distance (1.275 Å) is the same as in the free HCl molecule. The first-excited Π states of the HCl molecule are slightly affected by the surrounding Xe atoms, and consequently the transition energy to these states $T_{1\to2} - T_{1\to3} - 8.06$ eV is lower than in the case of the XeHCl van der Waals complex (8.28 eV) and the free HCl molecule (8.31 eV). The energy of transition to the HCl 2Σ state is found to be equal to $T_{1\to40} - 10.05$ eV, which is a bit higher than in the free HCl molecule (9.89 eV).

The nature of ionic states with electron transfer from the Xe atoms to the Cl atom clearly depends much more strongly on the Xe atoms than in the case of the excited HCl valence states. The system formed by a HCl molecule and twelve surrounding Xe atoms has 36 ionic states, with the Cl^- ion and the positive charge distributed among all twelve Xe atoms. Although the distribution is non-uniform, there are no states where one or two Xe atoms share more than half of the charge. In all states, save for $k - 15,16$, the Cl^- charge is close to $q_{Cl} - -1$, and the charge in the states $k - 15,16$ is $q_{Cl} - -0.75$. In all ionic states ($k - 4-39$), the H atom is neutral or almost neutral. The energies of the ionic states form almost a band with close-lying levels. The excitation energies from the ground state to these levels are arranged in the limits between $T_{1\to4} - 8.28$ eV and $T_{1\to39} - 9.54$ eV. The lower limit of the excitation energy 8.28 eV is much smaller than the transition energy to the ionic state in the van der Waals complex (9.3 eV).

The HCl potential curve is found to coincide with that of a free HCl molecule. Consequently, the HCl vibrational mode is the same as in a free HCl molecule. Rotational motion of the HCl molecule inside the Xe cage is impossible. The HCl molecule performs a transverse vibrational motion with $\hbar\omega - 0.013$ eV or $\lambda - 0.01$ cm.

B. HCl Excited k = 2,3 States

After the HCl molecule in the Xe matrix is excited to the molecule states of Π symmetry (k = 2,3), the H atom begins to move apart from the Cl atom. If one considers the motion of the H atom in the adiabatic approximation, i.e., with fixed heavy atoms Xe and Cl, then the H atom has a minimum energy point at a large HCl distance, 2.6 Å. However, the H atom can continue its motion and escape from the cage, since the potential barrier for escape is a little lower than the initial (R_{ClH} = 1.275 Å) k = 2,3 state energy. The barrier becomes much lower when the Xe atoms are allowed to be shifted by the approaching H atom. According to this finding, the excitation of the HCl molecule to the Π state leads to molecular dissociation and the formation of free Cl and H atoms in the Xe solid, if to exclude or rule out recombination.[53]

C. $Xe_{12}^{+}Cl^{-}H$ Ionic Molecules

The quasistable ionic molecules with electron transfer from the Xe atoms to the Cl atom are formed in many, if not all, of the k = 4-39 ionic states. In contrast to the case of the molecular k = 2,3 excitation, the excitation to ionic states, at least k = 4-6, does not lead to the dissociation of the HCl molecule in the matrix, since the H atom is bound to the Cl^{-} ion by polarization forces, forming $Xe_{12}^{+}Cl^{-}H$ molecules.

In the minimum energy $Xe_{12}^{+}Cl^{-}H$ configuration of the lowest ionic k = 4 state, the Cl^{-} ion forms together with two charged Xe atoms almost an isosceles triangle, like in the cage with the Cl^{-} ion,[32] with a Xe-Cl-Xe angle of 61.6° and distances R_{ClXe} = 3.24 Å and R_{XeXe} = 3.32 Å. The H atom is located outside the $Cl^{-}Xe_{2}^{+}$ triangle at a distance R_{ClH} = 1.57 Å. The charge of the Cl^{-} ion is q_{Cl} = -0.99, whereas the two strongly-bound Xe atoms bear together a charge of $q_{Xe_{2}}$ = +0.91. A relatively-large charge of q_{Xe} = 0.04 is on one of the other

Xe atoms, and the remaining nine Xe atoms share together q = 0.03. The H atom

bears only q_H = 0.01. The transition energy to the ground state is $T_{4 \to 1}$ = 6

eV.

The geometry and the electronic structure of the k = 4 ionic molecule in

the solid matrix is similar to that of the gas-phase $Xe_{12}^+ Cl^- H$ molecule. The

geometry of the $Xe_2^+ Cl^-$ triangle of the $Xe_{12}^+ Cl^- H$ molecule in the matrix, its

location in the cage and the distribution of charge resemble those of the

$Xe_{12}^+ Cl^-$ molecule in the cage.[32]

5. Conclusions

The main findings of our calculations are as follows:

(1) There are two XeHCl van der Waals complexes. One of these complexes

has a collinear XeClH geometry, whereas another one has a bent configuration.

The dissociation energy of these complexes is about 0.02 eV. The HCl molecule

forms with Xe atoms also van der Waals clusters $Xe_n HCl$ whose dissociation

energy per Xe atom increases with n up to 0.07 eV at n = 12. The HCl $\Sigma \to \Pi$

excitation energy in the $Xe_n HCl$ van der Waals complexes and clusters is only

slightly lower than in the free HCl molecule. The excitation energy to the

first ionic state (k = 4) with $Xe_n \to Cl$ electron transfer depends strongly on n,

decreasing from 13 eV for separated Xe + HCl to 9.3 eV in the XeHCl complex and

to 8.5 eV in the $Xe_{12} HCl$ cluster.

(2) An ionic molecule of collinear geometry $(HXe)^+ Cl^-$ is formed in the

ground state. This molecule is separated from the neutral XeHCl configuration

by a potential barrier of 0.41 eV and has a negative energy of -0.39 eV. An

ionic collinear molecule $(XeH)^+ Cl^-$ is formed in the first excited k = 2 state.

The decay barrier of this molecule is 0.18 eV. It emits at $\hbar\omega$ = 5.35 eV.

(3) A quasistable ionic molecule with strongly-bound atoms (ions) is formed in the k - 4 state. The dissociation energy of this molecule to H + Xe^+Cl^- is D_e - 1.26 eV. The molecule emits in the infrared region.

(4) Quasistable ionic molecules with a weak-bound H atom and Xe^+Cl^- molecule (D_e - 0.12-0.18 eV) are formed in the states k - 4-6. In spite of the weakness of the H interaction with Xe^+Cl^-, these ionic molecules emit UV light of much higher photon energy ($\hbar\omega$ - 7.3-7.5 eV) than in the separated Xe^+Cl^- molecule ($\hbar\omega$ - 4 eV).

(5) The HCl molecule in the Xe solid matrix has a fixed location, and its translation motion is restricted. The HCl vibrational frequency is the same as for a free molecule. The transverse vibrations of the HCl molecule in the Xe matrix produce emission at $\hbar\omega$ - 0.013 eV. The excitation energy to the HCl Π state is 8.06 eV, almost the same as in the Xe_8HCl and $Xe_{12}HCl$ clusters. This excitation leads to the dissociation and escape of the H atom from the cage. The excitation energies to the ionic states (k - 4-39) form a band with a lower limit of 8.3 eV. The excitation to the ionic states leads to the formation of the ionic $Xe_{12}^+Cl^-H$ molecule. This molecule in the lowest state (k - 4) emits at $\hbar\omega$ - 6 eV.

Acknowledgments

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Table 1

Parameters of stable and quasistable XeHCl systems: k - state number, θ - Xe-Cl-H angle, R - interatomic distances (in Å), q - atomic charges (in e), μ - dipole moment (in Debyes), E - system energy, D_e - dissociation energy for an atom detachment, T - transition energies to the lowest k - 1-3 states (E, D_e, T in eV).

		1n	2n	1i	2i	3i	4i	5i	6i
	k	1	1	1	2	4	4	5	6
	θ	78°	180°	0°	0°	26°	180°	132°	135°
	Xe-Cl	4.10	3.82	2.85	3.74	3.20	2.92	3.34	3.43
R	Xe-H	4.03	5.095	1.60	2.39	2.42	4.50	2.60	2.61
	Cl-H	1.275	1.275	4.45	1.35	4.83	1.58	1.45	1.45
	Xe	0	+0.001	+0.79	+0.66	+0.56	+0.93	+0.91	+0.88
q	Cl	-0.178	-0.180	-1.0	-0.78	-0.77	-1.0	-0.91	-0.88
	H	+0.178	+0.179	+0.21	+0.12	+0.21	+0.07	0	0
	μ	1.09	1.08	15.3	12.6	13.2	12.6	14.6	14.5
	E	-4.634	-4.633	-0.391	2.68	2.71	3.80	3.79	3.85
	D_e	0.019	0.018	0.41*	0.18*	1.26	0.18	0.18	0.12
	atom:	Xe	Xe			H	H	H	H
	1				5.35	0.78	7.50	7.33	7.45
T	2					0.56	1.40	0.96	1.00
	3					0.46	1.40	0.59	0.72

* potential barrier

Table 2

Dissociation energies D_e and excitation energies T (in eV) of the Xe_nHCl van der Waals complexes and clusters in the gas phase and the HCl molecule in a Xe solid (S).

n	0	1	1	2	4	8	12	S
D_e	-	0.019	0.018	0.062	0.172	0.493	0.851	0.234
D_e/n	-	0.019	0.018	0.031	0.043	0.062	0.071	-
$T_{1 \to 2}$	8.31	8.28	8.31	8.24	8.22	8.02	8.00	8.06
$T_{1 \to 4}$	13.05	9.40	9.30	9.12	8.97	8.60	8.52	8.24

Figure Captions

1. Geometry of the XeHCl system (see Table 1): (a) van der Waals complexes 1n and 2n; (b) ionic molecules 1i, 3i and 4i. The numbers stand for interatomic distances in Å and atomic charges.

2. Geometry of the ionic molecules $Cl^-(Xe_2H)^+$ and $Xe_2^+Cl^-H$ in the $k = 4$ state. The numbers stand for interatomic distances in Å and atomic charges.

In the figure (left diagram, labeled "ln"):

H +0.18
4.03
1.275
−0.18
Xe 4.1 Cl

ln

Right diagram (labeled "2n"):

−0.18 +0.18
3.82 1.275
Xe Cl H

2n

Fig 1b

1 i

3 i

4 i

Fig. 2
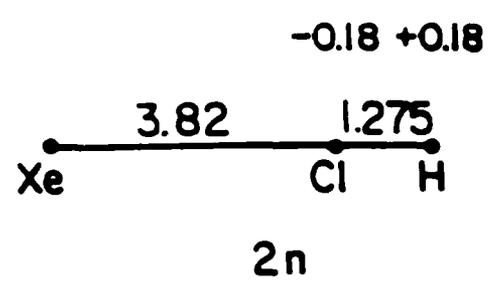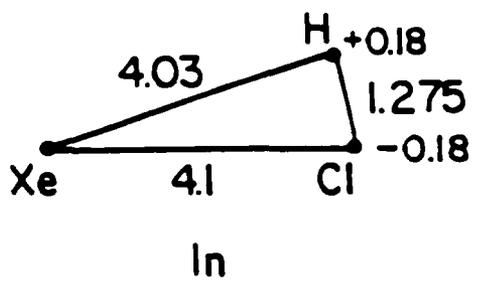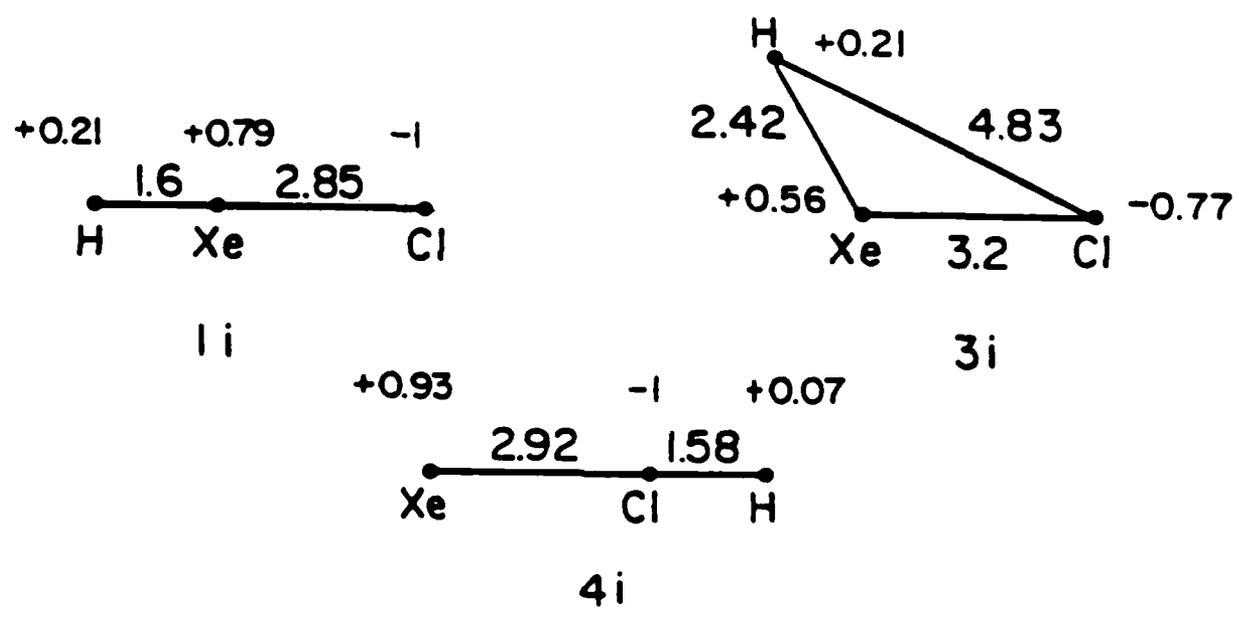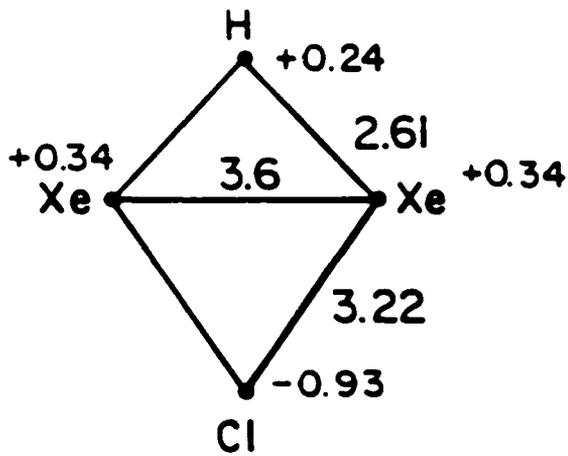
$Cl^-(Xe_2H)^+$
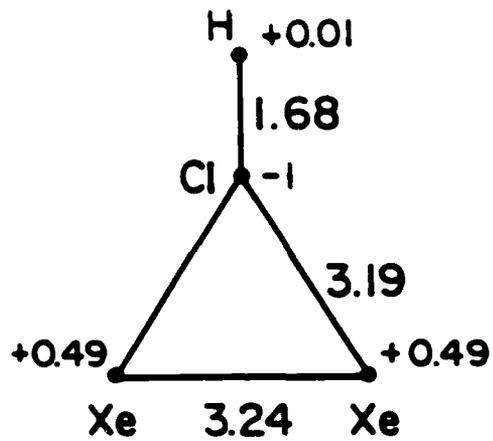
$Xe_2^+Cl^-H$

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