

Incipient chemical bond formation of Xe to a cationic silicon cluster: Vibrational spectroscopy and structure of the Si_4Xe^+ complex

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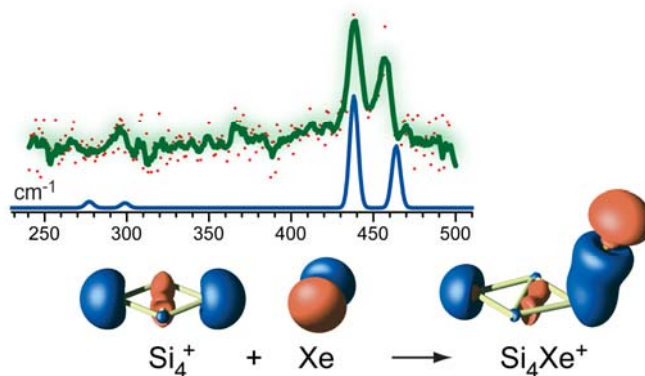
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Abstract

The size-selective vibrational spectrum of Si_4Xe^+ in the 240-500 cm^{-1} range has been recorded using infrared (IR) multiple photon dissociation spectroscopy. Comparison to linear IR absorption spectra of Si_4^+ and Si_4Xe^+ calculated using density functional theory including dispersion corrections reveals an important influence of the Xe ligand on the structure of the cluster, involving significant charge transfer and formation of an incipient chemical Si-Xe bond with $D_e=0.3$ eV.

- The IR spectrum of Si_4Xe^+ is obtained using infrared multiple photon dissociation
- Its spectrum differs from that predicted for bare Si_4^+ , indicating a distinct influence of Xe
- The interaction of Xe with Si_4^+ results in the formation of an incipient chemical Si-Xe bond



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1. Introduction

The messenger technique, where the evaporation of weakly bound ligands is used to probe the absorption of photons [1,2], has proven to be a powerful tool for the determination of size-specific absorption spectra of isolated gas-phase clusters from the ultraviolet to the infrared (IR) spectral range. In particular, spectroscopy in the IR energy range is very informative for obtaining insights into the cluster structure. IR vibrational spectra are a direct fingerprint of the atomic arrangement and allow, by comparison with theoretical spectra, detailed structural assignments. Often, rare gas atoms are used as messengers but small physisorbed molecules like H₂, N₂, or even O₂ have also been employed. Major advantages of the messenger technique include enhanced cooling and a substantial reduction of the dissociation energy of the cluster, leading to simpler and colder action spectra achieved with absorption of fewer photons as compared to the bare cluster [3-16].

For strongly bound clusters, it is often justified to assume that the weakly bound messenger does not significantly affect the intrinsic geometric, vibrational, and electronic properties of the cluster and has therefore only a minor effect on the IR spectra. The presence of the messenger can then be ignored in the in-detail analysis of the experimental spectra, and is thus also not accounted for in the theoretical modelling. This procedure largely simplifies the search for the carrier of the spectrum, and this combined experimental and theoretical approach has been very successfully applied recently for the structure determination of transition metal, metal oxide, or semi-metal clusters [8,9,13-15].

There are, however, certain examples where the influence of the messenger becomes more severe, and agreement between experimental spectra and theoretical predictions can be improved significantly or is only obtained if the messenger is explicitly taken into account [16-20]. Binding of the messenger may change the cluster's internal structure, or it can alter the energetic order of isomers, and thereby their relative abundance in the complex due to differences in the binding energy of the messenger. The magnitude of the perturbing effect may be tuned via the interaction strength of the messenger [6,21-23]. It usually depends on the polarizability and multipole moments and, e.g. for rare gases, increases with size. Using He or Ne can help to minimize such messenger effects [6-8,11,12,18,19,21].

Nevertheless, for experimental reasons it sometimes may be unavoidable to choose a heavy rare gas, like Xe, as ligand and it is therefore of interest to obtain a better understanding of its influence on the spectra and other properties of the cluster. The most extreme case of a messenger effect would be the formation of a strong covalent bond involving the rare gas atom as, e.g., observed in complexes with highly electrophilic, often (multiply) positively charged species [24-27].

Here we investigate the messenger's influence on the geometric, vibrational, and electronic structure for the complex of Xe with Si₄⁺ by analyzing its IR spectrum. We discuss the vibrational spectrum of Si₄Xe⁺ measured by IR multiple photon dissociation (IR-MPD). This complex has been

investigated before using UV-vis photodissociation spectroscopy [28] and there is a general consensus that the structure of bare Si_4^+ is a planar rhombus of D_{2h} symmetry [29-31]. This study complements previous work on larger cationic silicon clusters, Si_n^+ ($n=6-18$) [14], wherein it was found that for most sizes the experimental IR-MPD spectra obtained for the clusters' Xe complexes agree well with the computational IR spectra predicted for the lowest energy isomer of the bare Si_n^+ cluster. It was therefore concluded that Xe has only a minor influence on the appearance of the IR spectrum with respect to both band positions and intensities. In contrast, for Si_4Xe^+ we find qualitative differences between the measured spectrum and that predicted for bare Si_4^+ , which has motivated this detailed study of the interaction between Xe and Si_4^+ .

2. Experimental and Computational Techniques

All experiments are performed in a molecular beam setup installed at the beam line of the Free Electron Laser for Infrared eXperiments FELIX [32]. Details of the experimental procedures and data analysis have been reported previously [14,33]. Briefly, clusters are produced by laser ablation from a Si rod in the presence of a short pulse of He containing 0.5% ^{129}Xe . Complexes of the Si clusters with Xe atoms are formed in a copper channel held at ~ 90 K which is directly connected to the source. The distribution of cationic species emitted by the source is analyzed using a reflectron time-of-flight mass spectrometer. Prior to extraction of the clusters into the mass spectrometer, the molecular beam can be overlapped with the focussed IR beam from FELIX. Changes in the cluster distribution due to resonant absorption of IR photons and subsequent fragmentation of the Xe complexes are analyzed as a function of the IR frequency to yield mass selective IR depletion spectra. The depletion is converted to relative cross section.[33]

Density functional theory (DFT) calculations are performed within the Turbomole V6.2 program package [34], applying the def2-TZVP basis set [35] with the corresponding effective core potential for Xe, the Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA functional [36], and the resolution-of-identity approximation. To account for dispersion interactions, the 2nd version of the empirical correction after Grimme (DFT-D2) is used [37,38]. Without dispersion corrections the obtained structures and IR spectra are quantitatively very similar, and only the binding in the Xe complexes is calculated to be about 0.06 eV weaker. Harmonic IR spectra are calculated analytically and no frequency scaling is applied. All reported energies include zero-point vibrational energies. Atomic partial charges are determined from a natural population analysis.

3. Results and Discussion

The experimental IR-MPD spectrum of Si_4Xe^+ presented in Fig. 1a shows two distinct bands at 439 and 456 cm^{-1} in the spectral range investigated (240-500 cm^{-1}). To allow for an assignment, the measured spectrum is compared to linear IR spectra calculated for Si_4^+ and Si_4Xe^+ . The lowest energy isomer of Si_4^+ is a rhombus of D_{2h} symmetry (Fig. 2) and its calculated IR spectrum is shown in Fig. 1d. Although it exhibits a single intense band at 455 cm^{-1} , in the

vicinity of the experimentally observed doublet for Si_4Xe^+ , the splitting is not reproduced in the calculated spectrum. Certain higher lying isomers reported earlier [39], e.g., the Y-shaped or linear ones, are not identified as local minima within our theoretical approach and all converge to the D_{2h} symmetric structure. They are therefore not further considered here. Instead, we now turn the attention toward the influence of the Xe ligand.

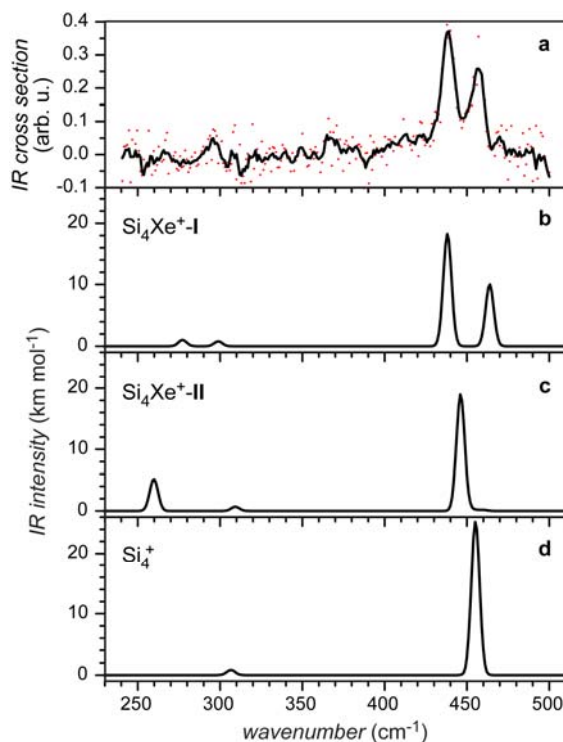


Figure 1. Experimental IR-MPD spectrum of Si_4Xe^+ (a) compared to linear IR absorption spectra calculated for two isomers of Si_4Xe^+ (b, c), and bare Si_4^+ (d) shown in Figure 2. Calculated spectra are folded with a Gaussian line shape function with 5 cm^{-1} full width at half maximum to facilitate convenient comparison to the experimental spectrum.

The rhombic Si_4^+ ion offers two distinctly different binding sites for the Xe ligand, namely i) at the lower coordinated Si atoms forming the acute apexes and ii) at Si atoms at the obtuse apexes (Fig. 2). The former leads to the calculated ground state structure of Si_4Xe^+ , denoted $\text{Si}_4\text{Xe}^+\text{-I}$, wherein the Si-Xe bond ($d_{\text{Si-Xe}}=307$ pm) is pointing out of the plane of the cluster. Its calculated binding energy is -0.30 eV. The Si_4 unit is only slightly distorted from free Si_4^+ ($\Delta d_{\text{Si-Si}} \leq 3$ pm), most noticeably it is buckled in the complex by about 3°. Interaction with Xe in the Si_4^+ plane is significantly weaker, and the planar transition state for inversion of $\text{Si}_4\text{Xe}^+\text{-I}$ is 0.16 eV higher in energy with $d_{\text{Si-Xe}}=362$ pm. In the second isomer, $\text{Si}_4\text{Xe}^+\text{-II}$, Xe is only bound by -0.18 eV, i.e. it is 0.12 eV above $\text{Si}_4\text{Xe}^+\text{-I}$. No other stable minimum has been located. The harmonic IR spectrum of $\text{Si}_4\text{Xe}^+\text{-II}$ is similar to that of bare Si_4^+ . The main band is only slightly red-shifted to 446 cm^{-1} and a second band at lower frequency (260 cm^{-1}) becomes prominent. Transitions below the experimentally investigated range are not discussed here but full spectral information is reported in

the Supporting Information (SI). In contrast to $\text{Si}_4\text{Xe}^+\text{-II}$, the IR spectrum of the lowest energy isomer $\text{Si}_4\text{Xe}^+\text{-I}$ agrees well with the experimental spectrum. Its prominent doublet at 438 and 464 cm^{-1} is close to the experimental peak positions (within 8 cm^{-1}) and also the intensity ratio is similar to that observed experimentally. It is therefore concluded that predominantly this isomer is present in the molecular beam.

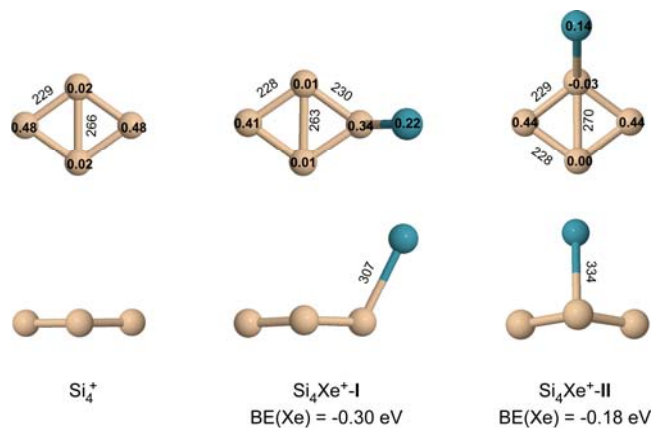


Figure 2. Structures and atomic charges (in e) of Si_4^+ (D_{2h}) and the two isomers of Si_4Xe^+ (C_s). Bond lengths are given in pm. The Si_4 unit in the Xe complexes is not planar but buckled by about 3° in $\text{Si}_4\text{Xe}^+\text{-I}$ and by 13° in $\text{Si}_4\text{Xe}^+\text{-II}$. All Cartesian coordinates are provided in the SI.

The preference for formation of $\text{Si}_4\text{Xe}^+\text{-I}$ can be rationalized by the rather unbalanced charge distribution in Si_4^+ (Fig. 2). The Xe atom interacts with one of the two outer Si atoms of the rhombus, which share essentially all of the excess charge of the cationic cluster. However, the bonding is not primarily due to charge-induced dipole interaction. In the complex, the Xe atom is partially charged by +0.22 e, while the charge on the nearby Si atom is significantly reduced from +0.48 to +0.34 e. The partial charge on the Xe ligand comes from a depletion of atomic p density and can be related to a bond formation to Si involving the Xe 5p orbitals. The interacting molecular orbitals of Si_4^+ and the atomic 5p orbitals of Xe are shown in Figure 3. Full electron transfer is energetically not feasible, as the ionization energy of Xe is 12.1 eV [40] vs. 8.2 eV for Si_4 [39]. In the $\text{Si}_4\text{Xe}^+\text{-II}$ isomer, the binding is much weaker, as the charge transfer is significantly smaller and does not involve the Si atom the Xe is directly attached to.

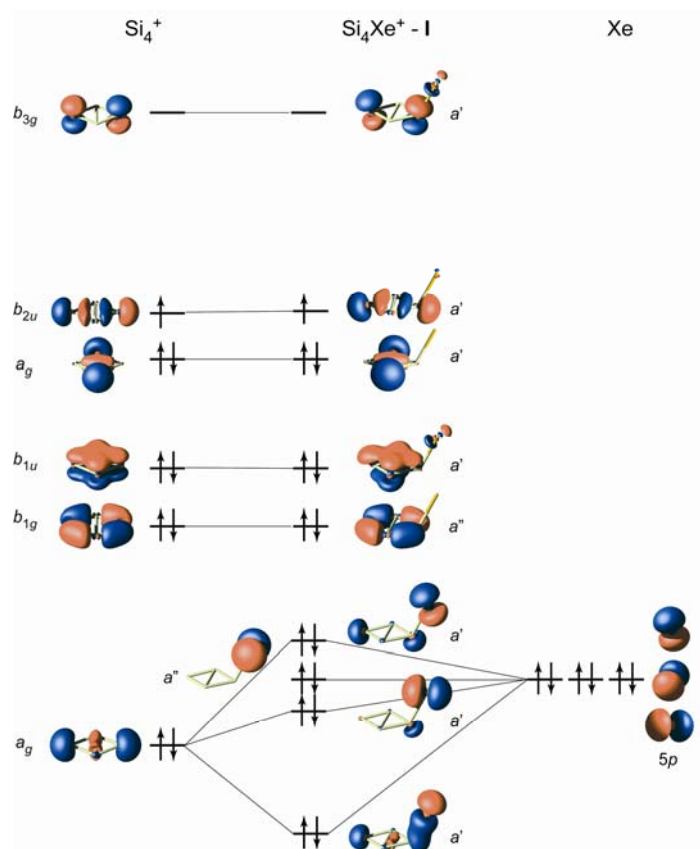


Figure 3. Energy level scheme and orbitals for the interaction between Si_4^+ (left) and Xe (right) leading to the formation of $\text{Si}_4\text{Xe}^+ - \text{I}$ (middle).

Due to the symmetry reduction from D_{2h} to C_s induced by Xe complexation, the concerted antisymmetric stretch (b_{2u} , 455 cm^{-1}) and breathing (a_g , 457 cm^{-1}) vibrations in Si_4^+ transform into two different stretch vibrations (a' , 438 cm^{-1} ; a' , 464 cm^{-1}) that now involve only half of the rhombus, i.e. they are localized at one Si triangle, respectively (Fig. 4). These modes carry substantial IR activity and are the ones observed in the experiment. Furthermore, due to the partial charging of the Xe atom, the modes involving a change in the Si-Xe bond length have comparatively high IR intensities. They should therefore be (easily) observable using the applied experimental technique, but are outside of the frequency range investigated.

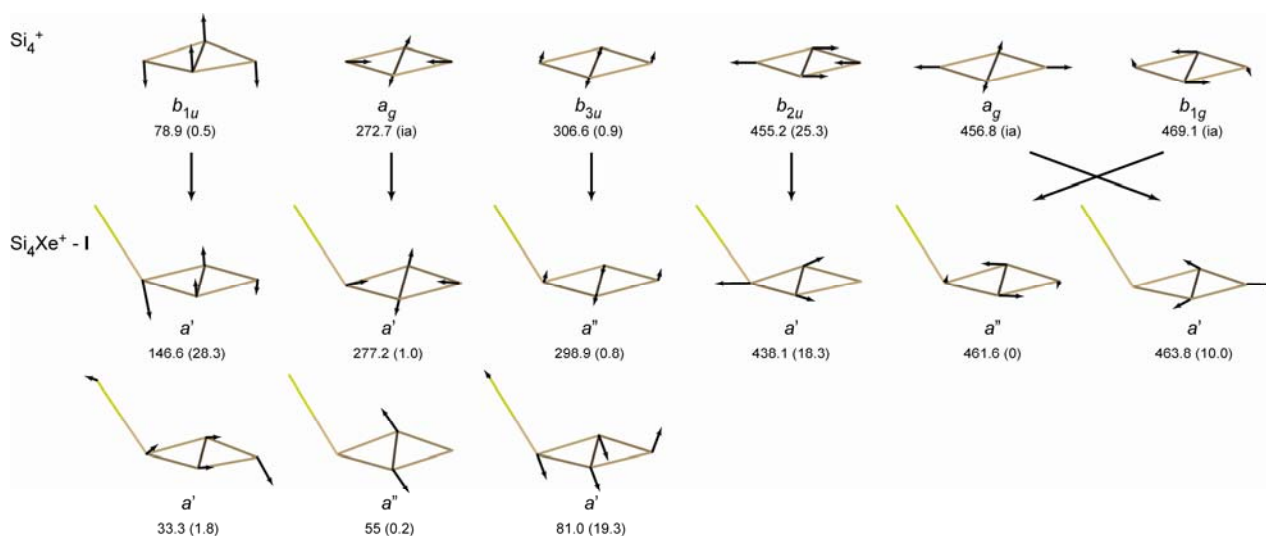


Figure 4. Representations of vibrational normal modes of Si_4^+ and $\text{Si}_4\text{Xe}^+-\text{I}$, their calculated vibrational frequencies (in cm^{-1}) and IR intensities (in km mol^{-1} , ia=IR inactive). The arrows illustrate how the six modes of Si_4^+ having D_{2h} symmetry map onto the modes of $\text{Si}_4\text{Xe}^+-\text{I}$ with C_s symmetry.

Finally, it is noted that, while the spectra of Si_6^+ and larger clusters up to $n=21$ have been obtained previously [14], no IR spectrum of Si_5^+ could be measured here and in the preceding experiments, although the Xe complex is formed in abundance comparable to the other sizes. However, our calculations reveal that all IR absorptions of Si_5^+ in its lowest energy structure (a trigonal bipyramid) are very weak, at maximum 5 km mol^{-1} , respectively 2.5 km mol^{-1} for transitions in the spectral range investigated here (see the SI). A similar argument may explain why a matrix isolation IR spectrum of neutral Si_5 is lacking, while those of other sizes have been reported [41].

4. Conclusions

The comparison of the experimental IR-MPD spectrum of the Xe messenger complex of Si_4^+ with the harmonic IR spectrum calculated for the rhombic ground state structure of Si_4^+ reveals significant differences. This observation is rationalized by the substantial perturbation of the Si_4^+ properties through the incipient formation of a chemical bond to the Xe atom. Two isomers of the Si_4Xe^+ complex are found, with the more stable one giving good agreement with the experimental findings. In this complex, we identify an interaction between an a_g orbital of Si_4^+ , which is essentially located at the two low-coordinated Si atoms, and the Xe 5p atomic orbital, leading to an overall reduction of electron density at the Xe atom. While in this complex the Xe atom is bound by only $\sim 0.3 \text{ eV}$, its presence leads to considerable modification of the IR spectrum compared to bare Si_4^+ . The example of Si_4Xe^+ demonstrates (once more) that even for relatively weakly bound complexes the presence of ligands, which are supposed to be merely inert spectators, may need to be taken into account explicitly in the computational analysis.

Acknowledgments

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