I. INTRODUCTION

Since 1995 a number of noble-gas hydride molecules with the general formula HNgY (where Ng=noble-gas atom and Y=electronnegative fragment) have been prepared in low-temperature matrices. Preparation of these HNgY molecules involves UV photolysis of HY precursors followed by thermal mobilization of H atoms in the noble-gas host. The first molecules prepared and characterized using this synthesis method were HXeCl, HXeBr, HXeI, and HKrCl. Recent findings include HArF, 4,5 open shell species HXeO (Ref. 6) and a group of organo-noble-gas molecules prepared from acetylene and diacetylene (HXeCCH, 7,8 HXeCC, 7 HXeCCXeH, 7 HKrCC, 9 HXeC2H, 10 and HKrC2H16). HXeCCH was first predicted computationally by Lundell et al. along with other large organic molecules such as Xe-insertion compounds of benzene and phenol. 11

The HNgY molecules are high-energy metastable species with respect to the H+Ng+Y asymptote, and they are formed from neutral H+Ng+Y fragments. Most of the significant studies on these molecules have been performed in noble-gas matrices, however, HXeI, HXeH, and HXeCl have also been reported in Xe clusters in the gas phase. An important question concerns the existence of the HNgY molecules without the stabilizing environment of the polarizable Xe or Kr host matrix. The first HNgY molecules prepared in a different noble-gas matrix were HXeCl and HXeBr in a Kr matrix. Lorenz et al. reported HXeCl and HXeBr in a Ne matrix and concluded from these results that these molecules should be intrinsically stable. 15 Stabilization and destabilization effects on the HXeOH molecules upon complexation with water have been studied theoretically and experimentally. 16 Due to the strong (HNg)\(^+\)Y\(^-\) ion-pair character, HNgY molecules have large dipole moments and, therefore, they are attractive systems to investigate electrostatic interactions with surrounding. 3,17,18

Recently, various computational and experimental studies on complexation of HNgY molecules have been reported. 16–23 Complexes of HXeOH with water molecules [HXeOH\(\cdot\cdot\cdot\)H\(_2\)O and HXeOH\(\cdot\cdot\cdot\)\(\cdot\cdot\cdot\)(H\(_2\)O)\(_2\)] produce a large experimental blueshift of >100 cm\(^{-1}\) for the H–Xe stretching frequency. 16 Similarly a strong blueshifting (>100 cm\(^{-1}\)) effect was observed for the H–Kr stretching mode in the HKrCl\(\cdot\cdot\cdot\)N\(_2\) complex 17,18 whereas other experimentally prepared HNgY complexes (HArF\(\cdot\cdot\cdot\)N\(_2\) and HKrF\(\cdot\cdot\cdot\)N\(_2\)) exhibit smaller blueshifts of the H–Ng stretching vibration. 18

Stabilization of HHeF molecule upon complexation with Xe atoms was studied computationally. 20 The calculations suggested that dissociation of HHeF via the H–He stretching coordinate might be suppressed and its lifetime increased by inserting HHeF into large Xe clusters or matrices. Additionally, various 1:1 HNgY\(\cdot\cdot\cdot\)N\(_2\) complexes have been calculated. McDowell studied computationally linear HHeF\(\cdot\cdot\cdot\)N\(_2\) complexes 35 and in an other study, he and Buckingham compared vibrational properties of FAH\(\cdot\cdot\cdot\)Ng and FH\(\cdot\cdot\cdot\)Ng complexes 36 (Ng=He, Ne, Ar, and Kr). Khriachtchev et al. calculated 1:1 HXeBr\(\cdot\cdot\cdot\)Xe complexes in a study of hindered rotation of HXeBr molecule. 23

In the present work, HXeCCH molecule is made in Kr and Ar matrix media in addition to the previous studies in Xe matrices. This is the first case when the organo-noble-gas compound is prepared in an Ar matrix. The matrix effects on the H–Xe stretching absorption of HXeCCH are reported. Using calculated 1:1 HXeCCH\(\cdot\cdot\cdot\)Ng complexes (Ng=Ar, Kr, and Xe), we analyze the interaction of the hosts with the embedded molecule. Also, experimental and computational data on acetylene-Xe complexes are presented.
We used acetylene typically 30 K for Xe matrices. The matrix thickness was cryostat were deposited onto a CsI window in a closed-cycle helium Kr, or Ar matrices were photolyzed with an excimer laser operating at 193 nm photolysis of a C₂H₂/Xe matrix with 600 pulses (−10 mJ/cm²) and 3900 pulses (−13 mJ/cm²) and the lower spectrum is a result of the 193 nm photolysis of a C₂H₂/Ar matrix with 600 pulses (−10–14 mJ/cm²).

II. EXPERIMENT

A. Experimental details

To prepare C₂H₂/Xe/Ng (Ng=Xe, Kr, or Ar) matrices, the gases were mixed in various proportions in a glass bulb. The matrix ratios were [C₂H₂]:[Xe]:[Ng]=1:(0−10):1000. We used acetylene (≥99%), Ar (Aga, ≥99.999%), Kr (Aga, ≥99.995%), and Xe (Aga, ≥99.999%). The samples were deposited onto a CsI window in a closed-cycle helium cryostat (DE-202, APD) at 20 K for Ar, 22–27 K for Kr, and 30 K for Xe matrices. The matrix thickness was typically ~100–200 μm. The IR absorption spectra (4000–400 cm⁻¹) were recorded at 8 K using a Nicolet 60 SX Fourier transform infrared spectrometer with 1 cm⁻¹ resolution coadding 500 scans. The C₂H₂/Xe/Ng (Ng=Xe, Kr, or Ar) matrices were photolyzed with an excimer laser (MPB, MSX-250) operating at 193 nm (ArF).

B. Experimental results

The IR absorption spectra of acetylene in Xe and Ar matrixes (C₂H₂/Xe and C₂H₂/Ar) and in an Ar matrix doped with Xe (C₂H₂/Xe/Ar) are presented in Fig. 1. These spectra agree with the previous measurements of Maier and Lautz in solid Xe and Andrews et al. in solid Ar.²⁴,²⁵ The spectra of mixed matrices (C₂H₂/Xe/Ng) show that Xe atoms interact with acetylene. The vibrational frequencies of acetylene in different matrix solids are presented in Table I. For the C₂H₂-Xe complexes, the monomer-to-complex shifts of the C–H stretching mode (ν₁) are up to −4.4 cm⁻¹ in Ar and −2.0 cm⁻¹ in Kr matrices. For the CC–H bending mode, only in an Ar matrix monomer-to-complex shifts are visible +5.6 and −0.2 cm⁻¹. In solid Kr, the CC–H bending absorption of acetylene becomes broader.

193 nm photolysis of a C₂H₂/Xe matrix produces mainly C₃H radicals (1852 cm⁻¹).²⁶ Xe–CC complexes (1767 cm⁻¹),²⁴ and XeHxe⁺ ions,²⁷ similarly to the previous experiments.²⁴,²⁵ The main photolysis products in C₂H₂/Ar and C₂H₂/Xe/Ar matrices are presented in Fig. 2. It can be seen in the IR absorption spectra that the CCH radicals (monomers at 1846.5 cm⁻¹ in Ar matrices)²⁹ interact with Xe atoms in an Ar matrix, and an additional band (~1842.5 cm⁻¹) is observed which is assigned to the CCH···Xe complex. Similarly upon photolysis of

TABLE I. Experimental absorptions of acetylene (in cm⁻¹). The shifts show the effect of Xe atoms in Ar and Kr matrices.

<table>
<thead>
<tr>
<th>Expt. results</th>
<th>C₂H₂/Xe/Ar</th>
<th>C₂H₂/Xe/Kr</th>
<th>C₂H₂/Xe/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H stretch (ν₁)</td>
<td>C₂H₂/Ar</td>
<td>C₂H₂/Xe/Ar</td>
<td>C₂H₂/Xe/Kr</td>
</tr>
<tr>
<td>(ν₁ + ν₃)</td>
<td>3302.8</td>
<td>3302.8</td>
<td>3293.3</td>
</tr>
<tr>
<td></td>
<td>3300.9</td>
<td>3300.9</td>
<td>3290.1</td>
</tr>
<tr>
<td></td>
<td>3289.1</td>
<td>3288.7</td>
<td>3280.1</td>
</tr>
<tr>
<td></td>
<td>3286.7</td>
<td>3286.7</td>
<td>3278.0</td>
</tr>
<tr>
<td></td>
<td>3284.7</td>
<td>3284.7</td>
<td>3266.5</td>
</tr>
<tr>
<td>CC–H bend (ν₃)</td>
<td>1334.8</td>
<td>1334.8</td>
<td>1326.5</td>
</tr>
<tr>
<td></td>
<td>1333</td>
<td>1333</td>
<td>1324.6</td>
</tr>
<tr>
<td></td>
<td>1330.9</td>
<td>1330.9</td>
<td>1327.5</td>
</tr>
</tbody>
</table>

Values are from Ref. 28.
Monomer.
The structures of the 1:1 C\textsubscript{2}H\textsubscript{2}\cdots Xe complexes presented in Fig. 5 are true minima on the computed potential energy surface. The complexation slightly elongates the H–C
and C–C bonds for both structures from their values for monomeric acetylene. The calculated IR absorption frequencies and intensities are presented in Table III. The monomer-to-complex shifts of the C–H stretching mode are −3.3 and −0.9 cm⁻¹ for the linear and bent complex structures, respectively. For the CC–H bending mode, the calculations show a significant difference in the monomer-to-complex shifts between these two complex structures. For the linear C₂H₂⋯Xe complex, the shift is +6.6 cm⁻¹, whereas for the bent C₂H₂⋯Xe complex it is −0.7 and −2.3 cm⁻¹. The computed interaction energies of the two stable C₂H₂⋯Xe complexes are presented in Table IV. The bent structure is energetically more favorable for the two structures by ~68 cm⁻¹.

For the 1:1 HXeCCH⋯Ng (Ng=Ar, Kr, and Xe) complexes, we found three configurations corresponding to the true energy minima on the computed potential energy surfaces. These configurations are similar to the reported Xe⋯HXeBr structures. One of the structures is bent [bent (A) complex]. The other two structures are linear [linear (B) and linear (C) complexes] where the Ng atom interacts with HXeCCH from the H–Xe and C–H ends, respectively (see Fig. 6 and Table V). The complexation in the case of the bent (A) and linear (B) complexes leads to a shortening of the H–Xe bond and to an elongation of the Xe–C bond compared with the monomer. For the linear (C) complex, the complexation elongates the H–Xe bond and shortens the Xe–C bond. The changes in bond lengths between complexes and monomer are small (~0.0009 Å). The calculated harmonic vibrational frequencies and IR absorption intensities are presented in Table VI. The complexation increases the H–Xe stretching frequency for almost all bent (A) and linear (B) complexes except for the bent Ar⋯HXeCCH complex. For the linear (C) complexes the complexation decreases the H–Xe stretching frequency. These complexation-induced spectral changes are similar to the previous results with the other HNgY systems.

The computed interaction energies of the HXeCCH⋯Ng complexes are presented in Table VII. The bent configurations (A) of HXeCCH⋯Ng are energetically more favorable than the corresponding linear configurations (B) and (C) at both levels of theory. The interaction energy of the bent Xe⋯HXeCCH complex is largest (~447.4 cm⁻¹) and for the linear HXeCCH⋯Kr it is smallest (~3.0 cm⁻¹) at the MP2 level. The calculations at the CCSD(T) also show that the bent Xe⋯HXeCCH complex is the most strongly bound (~416.4 cm⁻¹), but the weakest bound system is the linear Ar⋯HXeCCH complex (~94.5 cm⁻¹). The 1:1 HXeCCH⋯Ng complexes are rather typical van der Waals complexes picturing a rather weak interaction between the complex moieties. This is evident also by the fact that the HXeCCH subunit structure in the complex is almost unperturbed by the vicinal Xe atom, and the molecular partial charges change very little. A slight increase of ionicity in the general nature of HXeCCH is, however, found.

### IV. DISCUSSION

In the experiments, we used acetylene and Xe as precursors in solid Kr and Ar. Figure 1 shows the effect of doping with Xe atoms on the acetylene spectra in solid Ar. The Xe doping produces new spectral features for C₂H₂, which is due to C₂H₂⋯Xe complexation, and the H–Xe stretching complexation-induced bands are redshifted from the C₂H₂ monomer bands in both Ar and Kr matrices. The proportion of the C₂H₂⋯Xe complexes is larger for Ar than for Kr.
matrices, i.e., the complexation of C₂H₂ with Xe atoms is more efficient in Ar matrices. This is probably due to competing “complexation” with host atoms, which is presumably stronger for Kr than for Ar. The experimental shifts of the C–H stretching vibration are up to −4.4 cm⁻¹ in Ar matrices and −2.0 cm⁻¹ in Kr matrices, which agree with the calculations for the 1:1 C₂H₂⋯Xe complexes. The computed C–H stretching absorption shifts are −0.9 cm⁻¹ for the bent C₂H₂⋯Xe complex and −3.3 cm⁻¹ for the linear C₂H₂⋯Xe complex. For the CC–H bending mode, the observed experimental shifts are +5.6 and −0.2 cm⁻¹ in Ar matrices and no shift is observed in Kr matrices. For the bent C₂H₂⋯Xe complex, the calculated shift of the CC–H bending mode is −0.7 and −2.3 cm⁻¹ for the two split components, which basically agree with the experimental results. For the linear C₂H₂⋯Xe complex, the calculations give a blueshifted value (+6.6 cm⁻¹) for the CC–H bending mode, which is very close to the measured experimental value in an Ar matrix. This suggests that both configurations of C₂H₂⋯Xe are present in the matrix, even though the bent configuration is energetically more favorable of the two structures. In literature, several experimental and computational studies on C₂H₂⋯Ng (Ng=He, Ne, and Ar) complexes can be found. The calculations of Hasse et al. gave for C₂H₂⋯Ar complex T-shaped structures, and in a recent study, Munteanu and Fernández have calculated intermolecular ground-state potential energy surfaces of the C₂H₂⋯He, Ne, and Ar van der Waals complexes. Rutkowski et al. studied acetylene dissolved in liquefied Kr, Ar, N₂, CO, and CO₂ using IR absorption measurements and B3LYP and MP2 calculations. Their calculations predicted minima for the C₂H₂⋯B (B =Ar, N₂, CO, and CO₂) linear structures. The IR spectra of these systems suggest an increasing effect of anisotropic intermolecular interactions in the molecular solvent. Lorenz et al. have studied experimentally and computationally HBr⋯Xe and HCl⋯Xe complexes, which were observed after deposition of HBr/Xe and HCl/Xe samples in solid Ne. These HBr⋯Xe and HCl⋯Xe complexes were the precursors of HXeBr and HXeCl molecules in solid Ne, similarly to the present study, where the acetylene-Xe complexes are the precursors of HXeCCH.

The 193 nm photolysis of acetylene-Xe complex in Kr and Ar matrices yields HCC radicals and its complexes with Xe and also Xe⋯CC molecules (see Fig. 2). The HCC⋯Xe complexes are more visible in solid Ar than in solid Kr, i.e., the complexation with Xe is stronger in Ar matrices. This trend is in agreement with better C₂H₂⋯Xe complexation in Ar matrix. The photolyzed C₂H₂/Xe/Ng matrices were annealed to mobilize the H atoms in the lattice. The annealing makes possible the formation of HXeCCH molecules in the H+HCC⋯Xe reaction in Ar and Kr matrices. The HCC⋯Ng complex was not calculated because the results at the computational level used here could be unreliable for the open shell species.

The assignment of the observed novel bands to

![Diagram](https://example.com/diagram.png)

*FIG. 6. Computational structures of the HXeCCH⋯Ng complex. The geometry parameters calculated are presented in Table V.*

### Table III. Computational spectra of C₂H₂ monomer and C₂H₂⋯Xe complexes at the MP2(full) level of theory. The vibrational frequencies are in cm⁻¹ and IR intensities (in parentheses) are in km mol⁻¹. The shifts are calculated subtracting the frequencies of complex from the value of monomer.

<table>
<thead>
<tr>
<th>Computational results</th>
<th>C₂H₂</th>
<th>C₂H₂⋯Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Linear complex</td>
</tr>
<tr>
<td>C–H stretch (ν₁)</td>
<td>3534.2 (0)</td>
<td>3530.9 (2)</td>
</tr>
<tr>
<td>CC stretch</td>
<td>3447.0 (92)</td>
<td>3443.7 (139)</td>
</tr>
<tr>
<td>CC–H bend (ν₂)</td>
<td>1965.4 (0)</td>
<td>1963.8 (1)</td>
</tr>
<tr>
<td></td>
<td>738.1 (100)</td>
<td>744.7 (86)</td>
</tr>
<tr>
<td></td>
<td>592.0 (0)</td>
<td>599.5 (1)</td>
</tr>
<tr>
<td></td>
<td>37.4 (0)</td>
<td>43.2 (0)</td>
</tr>
<tr>
<td></td>
<td>34.5 (0)</td>
<td>19.3 (0)</td>
</tr>
</tbody>
</table>

 Degenerated bending modes.

### Table IV. MP2-computed interaction energies of the C₂H₂⋯Xe complex structures. The values are in cm⁻¹. [a]

<table>
<thead>
<tr>
<th></th>
<th>C₂H₂⋯Xe (bent)</th>
<th>C₂H₂⋯Xe (linear)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{int}</td>
<td>−226.2</td>
<td>−220.6</td>
</tr>
<tr>
<td>E_{int,ZPVE}</td>
<td>−205.5</td>
<td>−157.4</td>
</tr>
<tr>
<td>E_{int,CP}</td>
<td>−161.5</td>
<td>−135.8</td>
</tr>
<tr>
<td>E_{int,CP,ZPVE}</td>
<td>−140.8</td>
<td>−72.6</td>
</tr>
</tbody>
</table>

[a]Zero-point vibrational energy corrected interaction energy.

[b]Counterpoise corrected interaction energy taking into account the BSSE energy contribution.
HXeCCH molecules in Ar and Kr matrices is based on several experimental facts. The additional bands presented in Table II appear in Ar and Kr matrices only when Xe atoms are added to the gas mixture [see Figs. 3(e) and 4]. These bands are formed upon annealing of the photolyzed matrices containing the HCC···Xe species. In principle, this Xe-containing species could also be HXeCC because Xe–CC (precursor of HXeCC) is seen in the photolyzed matrices and the absorptions of HXeCCH and HXeCC are located in the same spectral region.

As the most probable candidate, we consider HXeCCH molecules rather than HXeCC radicals. For instance, HXeCCH and HXeCC can be distinguished from their different photostabilities. The HNgY molecules usually decompose easily upon irradiation in UV and in some cases in visible spectral regions. In the present case, the Xe-containing species in Kr and Ar decompose efficiently after 20 pulses (~10 mJ/cm²) at 193 nm (see Fig. 3), which is similar to HXeCCH in solid Xe. We irradiated the photolyzed and annealed (C₂H₂/Xe/Ar) sample at 488 nm from an Ar⁺ laser (~100 mW/cm² for 5 min). The species under discussion is stable under 488 nm irradiation, which is characteristic for HXeCCH whereas HXeCC is efficiently bleached by 488 nm radiation in 1 min time scale [see Fig. 3(a)]. It was found in Xe matrices that the HXeCCH to HXeCC proportion strongly depends on the 193 nm photolysis time of the deposited matrices. We used different photolysis periods for the C₂H₂/Xe in Ar and Kr matrices; however, this did not change the relative intensities of the annealing-induced bands shown in Fig. 3. These facts indicate that all bands in this region belong to the same absorber (HXeCCH). The CCH bending and CH stretching absorptions were not observed in the mixed matrices because they were too weak and they could not be used to distinguish between HXeCCH and HXeCC.

It is not absolutely clear why HXeCC radicals are not observed in these experiments; however, several reasons exist. First, we used photolysis at 193 nm, which was previously found to favor the HXeCCH formation. Second, photolysis of C₂H₂ and CCH can be a local process, and the formation of H₂ molecules can take place upon photodecomposition of CCH radicals. If H₂ molecules form upon photolysis, the formation of HXeCC needs global mobility of H atoms, which can be somewhat suppressed in the mixed matrices. Third, the Xe–CC molecule is computationally bent (148.6°), which can produce a barrier for the formation of a linear HXeCC molecule, and this slows down the reaction at lower annealing temperatures in Ar and Kr matrices. We observed in solid Kr (C₂H₂/Xe/Kr) that the HCC and HCC···Xe concentrations increase upon annealing. In the C₂H₂/Xe experiments, HCC and Xe–CC form during photolysis but annealing decreases the amount of these compounds because HCC and Xe–CC are the precursors for HXeCCH and HXeCC, respectively.

The observed increase of the HCC···Xe concentration during annealing in solid Kr shows that H atoms can react with XeCC molecules without the formation of HXeCC. It seems that an H atom reacts more likely with C than with Xe atoms of Xe–CC molecules, which leads to the HCC···Xe complexes.

Two H–Xe stretching bands of HXeCCH are observed in solid Xe [see Fig. 3(a), the lower trace]. The doublet structure of the H–Ng stretching mode is characteristic for the HNgY molecules, as seen, for example, in the case of...
A number of organo-noble-gas molecules (HXeCCH, HKrCCH, HXeCCH, and HKrCCH) show a more extensive H–Ng stretching band fine structure (up to five different ab-
H–Xe stretching frequency can vary up to 10.8 and 7.6 cm$^{-1}$. For HXeBr, the observed splitting between H–Xe stretching bands is 5.7 cm$^{-1}$. Our calculations on 1:1 HXeCCH in solid Xe, the interval between two H–Xe stretching bands is 5.7 cm$^{-1}$. Our calculations on 1:1 HXeCCH···Xe complexes give spectral shifts up to 5.3 cm$^{-1}$ and the splitting can be explained by specific interactions of the HXeCCH molecule with Xe atoms in certain local morphologies. The present results are consistent with the conclusions of Ref. 28 that the two close H–Xe stretching bands are attributed to matrix sites. A similar doublet in the H–Xe stretching region is visible for HXeCCH in Kr and Ar matrices as well [see Figs. 3(b) and 3(c), respectively]. The experimental splitting of the H–Xe stretching doublet of HXeCCH is $\sim 13$ cm$^{-1}$ in solid Kr and $\sim 14$ cm$^{-1}$ in solid Ar. The calculations on the H–Xe stretching mode of 1:1 HXeCCH···Kr and HXeCCH···Ar complexes show that the H–Xe stretching frequency can vary up to 10.8 and 7.6 cm$^{-1}$ depending on structures of the HXeCCH···Kr and HXeCCH···Ar complexes, respectively. The observed splitting in solid Kr is quite close to the computed value on the HXeCCH···Ar complexes, but the correspondence between experiments and calculations is worse in the case of Ar, however, still acceptable. Furthermore, the calculations describe 1:1 complexes in a vacuum whereas the experiments are performed in the solid phase, and the solid surrounding can modify the geometry and the relative energies of the interactive molecular systems. The increase of the Xe/Ng ratio broadens the H–Xe absorption bands as it is seen in Fig. 3(c), which could be explained by a change of matrix morphology. This effect was seen also previously in systems such as HKrCl···N$_2$ in solid Kr (Ref. 17) and HXeBr in solid Xe, but the atomistic level mechanisms behind these observations are still unresolved.

The matrix effects generally include not only relatively small matrix-site splittings but also larger matrix-induced shifts due to more extensive interactions with the matrix material described as solvation effects. In our case, HXeCCH molecule can interact with different lattice atoms depending on the host matrix material (Xe, Kr, and Ar). For the H–Xe stretching absorptions, the highest frequency is found in solid Ar (1531.3 cm$^{-1}$) and it is almost 13 cm$^{-1}$ higher than that obtained in solid Kr and $\sim 45$ cm$^{-1}$ higher than that in solid Xe. This indicates that the stabilization of the H–Xe stretching bond is stronger in Ar than in Kr or Xe matrices. We try to understand if a single atom interaction to HXeCCH molecule could explain the observed shifts between HXeCCH in Xe and HXeCCH in other matrix media (Kr or Ar). The calculations performed on the 1:1 HXeCCH···Ng (Ng=Ar, Kr, and Xe) complexes show that the interaction energies for these systems are small (maximum $-444.7$ cm$^{-1}$) and the computational complexation-induced spectral shifts are quite different from the obtained solvation effect. It can be seen in Table VI that the computed complexation-induced shifts vary from $-1.2$ to $+6.4$ cm$^{-1}$, from $-1.4$ to $+9.4$ cm$^{-1}$, and from $-1.8$ to $+3.5$ cm$^{-1}$ for HXeCCH···Ar, HXeCCH···Kr, and HXeCCH···Xe complexes depending on the configuration, respectively. The calculations give the most blueshifted value for the H–Xe stretching vibration of the linear Kr···HXeCCH complex (B), whereas the largest experimental blueshift is found in an Ar matrix (see Table II). This means that the calculations on the 1:1 complexes are relevant to the matrix-site structure of HXeCCH as discussed above, but they are unable to describe the observed shift of HXeCCH between various matrix materials. To describe the solvation effect, the calculations should be done for much bigger HXeCCH···Ng$_n$ systems, and even dynamical effects should be probably included. The previous studies on HXeCl, HXeBr, and HXeCN molecules prepared in solid Kr are comparable with our present results. The H–Xe stretching absorption of HXeCl measured in solid Kr is shifted by $+15$ cm$^{-1}$ as compared to Xe matrices and this shift is $+20$ cm$^{-1}$ for HXeBr and $+26$ cm$^{-1}$ for HXeCN. For HXeCCH in solid Kr, the maximum shift of

**TABLE VII.** Electronic interaction energies and vibrational BSSE and ZPVE-corrected electronic interaction energies of the Ng···HXeCCH complexes obtained at MP2 level. The values are in cm$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>Ar···HXeCCH [bent (A)]</th>
<th>Ar···HXeCCH [linear (B)]</th>
<th>HXeCCH···Ar [linear (C)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{int}}$ (MP2)</td>
<td>$-305.8$</td>
<td>$-106.2$</td>
<td>$-164.0$</td>
</tr>
<tr>
<td>$E_{\text{int}}$ (CCSD(T))</td>
<td>$-207.4$</td>
<td>$-94.5$</td>
<td>$-164.7$</td>
</tr>
<tr>
<td>$E_{\text{int}}$ (MP2) $-\text{ZPVE}$</td>
<td>$-153.4$</td>
<td>$-38.3$</td>
<td>$-12.9$</td>
</tr>
<tr>
<td>Kr···HXeCCH [bent (A)]</td>
<td>$-471.4$</td>
<td>$-193.8$</td>
<td>$-271.7$</td>
</tr>
<tr>
<td>Kr···HXeCCH [linear (B)]</td>
<td>$-335.8$</td>
<td>$-164.1$</td>
<td>$-256.3$</td>
</tr>
<tr>
<td>HXeCCH···Kr [linear (C)]</td>
<td>$-249.5$</td>
<td>$-16.2$</td>
<td>$-3.0$</td>
</tr>
<tr>
<td>Xe···HXeCCH [bent (A)]</td>
<td>$-627.5$</td>
<td>$-249.8$</td>
<td>$-242.2$</td>
</tr>
<tr>
<td>Xe···HXeCCH [linear (B)]</td>
<td>$-416.4$</td>
<td>$-194.6$</td>
<td>$-215.2$</td>
</tr>
<tr>
<td>HXeCCH···Xe [linear (C)]</td>
<td>$-444.7$</td>
<td>$-168.4$</td>
<td>$-106.0$</td>
</tr>
</tbody>
</table>

*MP2-computed equilibrium structures are used in calculations.*
the H–Xe stretching frequency is +32.3 cm\(^{-1}\) from the value in solid Xe. It should be noted that in solid Ar, we also observed redshifted (4–6 cm\(^{-1}\)) absorption bands as compared with solid Xe (see Table II). The redshifted bands possibly originate from the presence of vicinal vacancies. As an exciting observation, Lorenz et al.\(^{15}\) have prepared HXeCl and HXeBr molecules in solid Ne. In their study, the H–Xe stretching absorption bands of HXeCl and HXeBr measured were redshifted by \(-\sim 36\) and \(-\sim 54\) cm\(^{-1}\) from the values in Xe matrices, respectively. It is unclear at the moment why the H–Xe stretching frequencies increase in Ar and Kr matrices and decrease in Ne matrices compared to Xe matrices. The computational efforts to model the trapping site effect on the atomistic level by including more Xe atoms in the quantum chemical model applied here, by combined QM/MM or classical MD simulations, are beyond this study and represent a challenge for the computations in the future.

V. CONCLUSIONS

HXeCCH molecules were prepared from C\(_2\)H\(_2\) and Xe in solid Kr and Ar matrices and characterized by IR absorption spectroscopy. The experimental data show that HXeCCH can form in other surroundings than a polarizable Xe environment. Two new annealing-induced absorptions were found at 1518.7 and 1505.6 cm\(^{-1}\) and one weaker absorption in solid Ar and Kr matrices and characterized by IR absorption bands as compared to solid Xe (see Table II). The redshifted bands possibly originate from the presence of vicinal vacancies. As an exciting observation, Lorenz et al.\(^{15}\) have prepared HXeCl and HXeBr molecules in solid Ne. In their study, the H–Xe stretching absorption bands of HXeCl and HXeBr measured were redshifted by \(-\sim 36\) and \(-\sim 54\) cm\(^{-1}\) from the values in Xe matrices, respectively. It is unclear at the moment why the H–Xe stretching frequencies increase in Ar and Kr matrices and decrease in Ne matrices compared to Xe matrices. The computational efforts to model the trapping site effect on the atomistic level by including more Xe atoms in the quantum chemical model applied here, by combined QM/MM or classical MD simulations, are beyond this study and represent a challenge for the computations in the future.

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