Interactions between Molecular Hydrogen and Alkali Halide Ion-Pairs in Neon Matrices

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Neon matrices of the alkali halide ion-pairs and H_2 give evidence of associations as characterized by infrared absorptions in the H−H stretching region. With the exception of KF, none of the absorptions correlated with analogous species in argon matrices. It was exceedingly difficult to obtain the 1:1 complex of $MX:H_2$ because of the extreme mobility of H_2 in the developing matrix, and concentrations of less than 70 ppm were necessary to achieve adequate dilution. LiI, LiCl, and CsF all induce infrared intensity in H_2 that is at higher wavenumber than what is seen in argon, and it is argued that the differences are due to an interaction which is fundamentally different from what is seen in argon. While it has been argued that dihydrogen interacts exclusively with the anion of alkali halides in argon, it is clear from these spectra that there must be at least some cation interaction as well.

Introduction

Hydrogen has been observed by infrared methods in zeolites; the site of attachment has been presumed by some to be at the cation.[1] However, Kostov and Kazansky have observed the spectra of cation-exchanged zeolite MX, where M represents a Group 1 cation, and have found very little variation of the frequency of the H−H stretching vibration as a function of the size of the cation.[2] This led them to believe that interactions might occur between dihydrogen and the cation at the same time that there were interactions between dihydrogen and negatively charged framework oxygen atoms. It is attractive to consider the position of the H−H stretching vibration as diagnostic of the interaction. In complexes with transition metal centers, the position of the H−H stretching vibration is red-shifted typically by over 1000 cm^{-1}.[3] Especially, when the shift of the H−H stretch is large, there can be substantial mixing of the H−H stretching mode and M−H stretching vibrations.[4] When the interaction is less strong, can the H−H stretching vibration be treated as an isolated mode and used as a metric for the mode of coordination and the degree of interaction? We attempt to address this question in what follows.

There are no unambiguous observations of dihydrogen associated with cationic sites in which the interaction is largely electrostatic. There is a great deal of covalency in the interaction of H_2 and CuCl.[5,6] A weak feature was observed in spectra of neon mixtures of H_2 and HF, but it is not clear whether the site of attachment is at hydrogen or at fluorine.[7] When H_2 is co-deposited with alkali halides in argon matrices, the infrared spectra show evidence of an interaction between the anion of the alkali halides and dihydrogen.[8,9] The position of the H−H stretching vibration falls within 3 cm^{-1} in the series MCl, where M = Li, K, Rb, and Cs.[8] Such consistency suggested that the chloride was the site which perturbed the dihydrogen. Since it would have been reasonable to expect an interaction with the cation, we have attempted to model these systems by ab initio techniques.[6] It was found that argon successfully competed at the cation side of the ion pair; the electronic energy component of the dissociation energy of Ar:NaCl, for example, was slightly more negative than that of H_2:NaCl.[6] Moreover, the zero-point energy contribution to the reaction favored the coordination of Ar over that of H_2. Recognizing that the argon, which was used as the matrix, interfered with interactions between cations of alkali halides and H_2, we undertook an investigation of neon matrices with the hope that we could characterize molecular hydrogen which is perturbed predominately by the cation.

Experimental Section

When matrices containing Ne, H_2, and alkali halides were deposited using the Displex model HC-2, temperatures were recorded between 6 and 8 K. These temperatures exceed the 4 K temperatures that are usually used for neon matrices; in fact, matrices are so volatile at 10 K that thermal insulation is typically lost. Matrices were deposited on a CsI disk of 25 mm diameter, a substantial portion of which was masked by the sample holder. An oval slot approximately 12 mm × 6 mm was left open. Matrices were deposited on the side of the crystal which was in contact with the part of the holder that was anchored into the tip of the Displex. Heat conduction between the holder and the crystal were facilitated with indium gaskets. Neon was obtained from Praxair and was 99.9983% pure. Hydrogen was obtained from Praxair at 99.995% pure. Deuterium was from BOC and 99.7% pure, while HD was obtained from Merck, Sharp and Dohme at a purity of 97%.

The deposit conditions are such that the resulting neon matrices were well-annealed as evidenced by the absence of significant light scattering. Flow rates of approximately 0.7 mmol/h could be accommodated. To be able to assign a feature in the H−H stretching region to a 1:1 species $MX:H_2$, we required the observation of the M−X stretch in the position of MX in pure neon matrices. With measurable quantities of MX lacking any association with H_2, it is probable that there will also be reasonably large quantities of the 1:1 complex. Hydrogen concentrations usually had to be less than about 70 ppm on a mole basis in order to still be able to see the uncomplexed MX, although this depends on the amount of alkali halide present.

Alkali halides were obtained from the following sources and were 99% pure or better: LiI, Aldrich Chemical, 99.99%; LiCl, Baker, 99.7%; KF, MCB, 99.0%; CsF, Aldrich Chemical,

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TABLE 1: Calculated Equilibrium Vapor Pressures of Alkali Halides[a]

salt	temp (°C)	vapor pressure (10^{11} atm)
LiI	440	4.4
	470	12.7
	500	33.7
LiCl	460	2.6
	500	33.7
	540	34.0
	625	331
KF	580	37.7
	625	127
	650	220
CsF	527	20.0
	580	89.8
	610	194

[a] Enthalpies and entropies of formation for the solid and gaseous ion-pairs obtained from ref 10.

99.9%. For evaporation, the alkali halide was contained in a small quartz test tube, the end of which was restricted to about 1−2 mm. The vessel was placed in a resistively heated quartz tube approximately 20 cm from the matrix site. The heating wire was wound more densely closest to the matrix site so that the gaseous alkali halide was heated to higher temperatures following evaporation. It was hoped that this would eliminate aggregation of ion-pairs in the gas phase. The heated region extended to within 5 cm of the cold end and 2 cm to where matrix gases were admitted. Temperatures of the quartz container were measured by using a chromel/alumel thermocouple attached to the vessel with wire.

The LiI was handled in an N_2-filled glovebox. The other alkali halides were handled in the air and all were outgassed in vacuo at temperatures approximately the same as those used for deposits. Ordinarily, the initial deposits still showed higher levels of CO_2 and H_2O impurities.

Spectra were recorded with 1 cm^{-1} resolution by using a Perkin-Elmer model System 2000 with a CsI beam splitter using medium Beer Norton apodization. The beam path was purged with dry nitrogen. The vibrations of the Displex resulted in anomalous peaks in the region 700−250 cm^{-1} at regular intervals making it difficult to characterize the M−X stretching region. Spectra are the result of signal-averaging of either 100 or 200 scans, taken 100 at a time.

Results and Discussion

Although it is not possible to know the concentration of alkali halide ion-pairs in the matrix, it is possible to achieve similar concentrations of the various alkali halides since the vapor pressures are known. Free energies of formation of gas and solid were used to calculate approximate vapor pressures for the alkali halide ion-pairs under the relevant conditions as shown in Table 1.[10] Linear interpolations were made between data separated by 100 °C.

LiI. Matrices were formed from LiI vapors originating from a cell that was heated from 440 to 500 °C. Features were observed in the Li−I stretching region which are assigned to the monomer ion-pair at 490.5 cm^{-1} with a shoulder at 492.8 cm^{-1}. This corresponds to the argon position of 447.5 cm^{-1} and the vapor phase of 498.2 cm^{-1}.[11] Peaks at 411.6 and 430.4 cm^{-1} were more prominent when the concentration of LiI was greatest and should be assigned to aggregates of LiI.

Figure 1 shows the spectrum produced by H_2-doped matrices of LiI with a sublimation temperature of 470 °C. Figure 2 shows a comparison of spectra with H_2, HD, and D_2. Table 2 gives the positions of the principal bands and correlated features from HD and D_2-containing matrices. Surprisingly, clear intensity is evident at 4110 and 4100 cm^{-1}, even with no added dihydrogen. We are persuaded that these features are due to impurity dihydrogen from the vacuum system. In all experiments involving alkali halides and "pure" neon, features appear at the appropriate positions for matrices containing dilute dihydrogen, even when no dihydrogen has been consciously added.

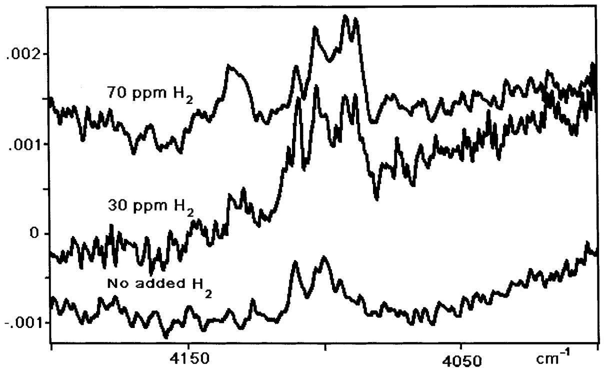

Figure 1. LiI in neon matrices. Sublimation temperature, 470 °C.

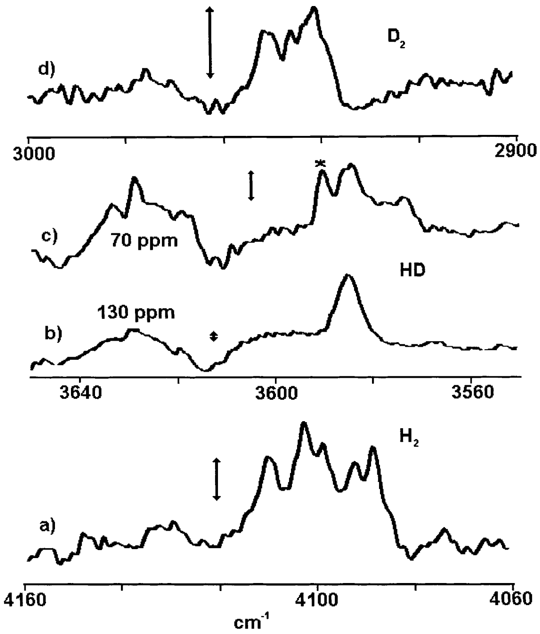

Figure 2. LiI in neon matrices doped with H_2, HD, and D_2. Double arrows define 0.001 absorbance units. For (a), (c), and (d), the hydrogen concentration is 70 ppm and the sublimation temperature is 470 °C. For (b), the hydrogen concentration is 130 ppm and the sublimation temperature is 500 °C. For (b) and (c), the asterisk marks the position of an impurity peak in the HD stretching region. The dip at 3614 cm^{-1} is the Q branch of a combination band of gaseous CO_2. Atmospheric water bands in the region of the H−D stretch were removed by tweaking the subtraction of the background spectrum. For (d), C−H stretching features associated with pump oil have been removed by subtraction of a spectrum of a neon matrix which contained no D_2.

In the LiI/H_2/Ne system, the features seen in "pure" neon in the H−H stretching region are joined by others at higher dihydrogen concentration. We assign the features seen at lowest dihydrogen concentration to the 1:1 complex. These features become relatively less prominent as the concentration of H_2 becomes highest. In the Li−I stretching region, there is relatively large intensity at 490 cm^{-1}, the position of the Li−I stretch when no dihydrogen is intentionally added. This feature is less prominent at higher concentrations of H_2 but its intensity does not correlate with features in the H−H stretching region that

TABLE 2: Positions of Infrared Absorptions in Neon Matrices (in cm^{-1})

LiCl			LiI		
H_2	HD	D_2	H_2	HD	D_2
4133p[b]		2974[a]	4135p[b]		2975[a]br
4128sh,p			4130p		
4123m		2961m	4110m	3591[c]	2950m
4116m	3596m		4100m	3584m	2944m
4111p			4098p		2942p
	3591[c]	2948p	4095p		
4097p	3586p	2946p	4092p	3578p	
			4088p	3574p	2938p
	3581p				
	3578p				

[a] Position is similar to the argon position for D_2 in argon; see, for example, ref 13. [b] "p" designates peaks assigned to aggregates containing more than one dihydrogen; "m" designates peaks assigned to aggregates containing a single dihydrogen. [c] Position is coincident with an unidentified impurity band and may not be due to LiX:$(HD)_x$

TABLE 3: Positions of Infrared Absorptions in Neon Matrices

	KF in cm^{-1}		CsF in cm^{-1}	
H_2 concn	H_2	D_2	H_2	D_2
≤70 ppm	4012			
	4015	2879		
		2893		
		2897		
	4056		4059	2913
	4062		4064	
	4084		4073	2923
	4089		4079	
	4094			
	4099			
>100 ppm	4074			
	4083		4084	
	4086			
	4095		4096	
	4099		4100	
			4106	
	4118			

are assigned to the 1:1 complex. From this behavior, we infer that the species at 490 cm^{-1} is due to an ion-pair with no near-neighbor dihydrogen. We have not been able to assign any feature in this region to the Li−I stretch of a species involving dihydrogen.

We have asserted that the 1:1 complex, LiI:H_2 gives both 4110 and 4100 cm^{-1}. It is highly unlikely that impurity dihydrogen can be so common as to give a bis-dihydrogen complex. If the dihydrogen concentration is increased while keeping the LiI concentration constant, other features become more prominent which presumably arise from the presence of multiple molecules of hydrogen. On the other hand if the LiI concentration is increased as shown in Figure 3, features of the 1:1 complex can still be prominent, even with relatively high H_2 concentrations. In Figure 3, the spectrum of the 1:1 complex is relatively free of complicating features of multiple-H_2 containing species when the sublimation temperature is highest. This can be understood if one assumes that dihydrogen is mobile in the developing matrix. It scouts out its environment until it locates a LiI ion-pair. With the larger concentration of ion-pairs, a molecule of hydrogen is quickly immobilized and very few hydrogen molecules will ever find an ion-pair that already has a dihydrogen. Conceivably, a molecule of hydrogen is not retained in the matrix if it does not associate with an ion-pair. No features are ever seen in the region 4140 cm^{-1} where *o*- and *p*-dihydrogen adsorb in argon. Interestingly, a feature is seen at 2974 cm^{-1} in the spectrum of deuterium-containing matrices, suggesting that deuterium is retained. Since the boiling point of dideuterium is 4 K higher than diprotium, it should be easier to trap. It is worth noting that dihydrogen concentrations of approximately 1000 ppm were necessary to give observable quantities of the 1:1 adduct of alkali halides in argon matrices.[8,9] To form adducts in matrices, usually both reactants cannot be dilute. To be able to observe features at 70 ppm or less in neon can only happen if one accepts that dihydrogen is mobile in the developing neon matrix.

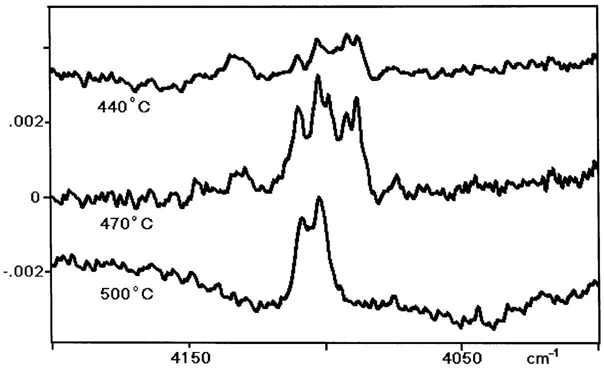

Figure 3. LiI in neon matrices doped with 70 ppm H_2.

From Figure 3, it can also be argued that the concentration of LiI ion-pairs generated at 440 °C is also on the order of 70 ppm or less in order for the 1:1 complex to play such an insignificant role in the product mixture, i.e., there is more than enough dihydrogen at 70 ppm to form multi-dihydrogen complexes. By 500 °C, the concentration of LiI will be roughly 10 times what it was at 440 °C and there are probably more LiI ion-pairs present than dihydrogen molecules for there to be such a predominance of the 1:1 complex. It can also be argued that ion-pair dimers and higher aggregates probably do not give spectral features in the region of 4100 cm^{-1}, otherwise one would expect increased complexity when higher sublimation temperatures are used when LiI oligomeric species are more common. Yet, it is clear from the bottom spectrum of Figure 3 that the spectrum is quite clear of features except those assigned to the 1:1 complex.

It is attractive to assign the features at 4110 and 4100 cm^{-1} to *o*-H_2 and *p*-H_2 associated with LiI, except the splitting is larger than what is observed for uncomplexed diprotium.[12,13] Alternatively, the bands are due to site splittings or the existence of several isomers of the 1:1 complex. A splitting of 10 cm^{-1} has been observed for hydrogen on sodium chloride surfaces where it was possible to characterize the spectrum with enriched *p*-H_2.[14] Experiments with HD are helpful in assigning the spectrum. In Figure 2c, the HD stretching region gives multiple absorptions, while in Figure 2b only a single peak is prominent at 3584 cm^{-1}. By subliming LiI at 500 °C, one expects a preponderance of the 1:1 complex as seen also in Figure 3. That only a single peak can be assigned to the 1:1 complex is readily understood if the splitting in the diprotium spectrum is due to the presence of ortho-para isomers. For the splitting to be larger than the 6 cm^{-1} observed in the gas phase, *o*-H_2 may bind the alkali halide more tightly than *p*-H_2. Analogous binding behavior has been observed for H_2HF.[15] Although there are other bands produced by HD, they correlate with features which are to the red of 4100 cm^{-1}. A ubiquitous band at 3591 cm^{-1} belongs to an impurity, possibly due to water bound to LiI.[16] A similar feature is seen in the spectrum of LiCl.

It is of interest to compare the spectrum of the 1:1 complex with what is observed in argon where the H_2 undoubtedly would

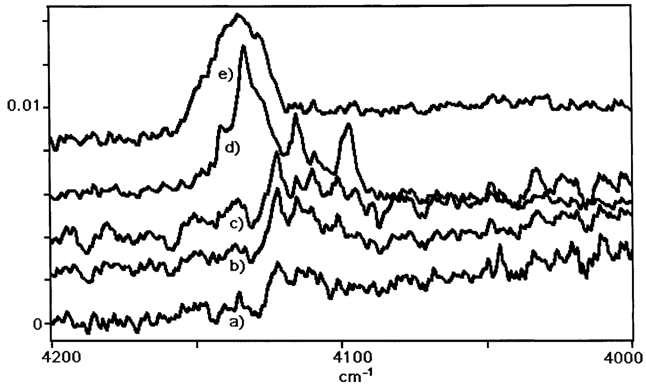

Figure 4. Neon matrices containing LiCl and (a) no added dihydrogen, sublimation temperature at 540 °C; (b) and (c) 70 ppm H_2, sublimation temperature at 540 and 510 °C, respectively; (d) 140 ppm H_2, sublimation temperature 500 °C; and (e) 660 ppm H_2, sublimation temperature at 500 °C.

bind at the iodide. We undertook to isolate LiI in argon matrices containing H_2. However, no intensity was observed in the H−H stretching region, even at concentrations as high as 4 mole percent of H_2, suggesting that argon successfully excludes dihydrogen from all sites.

LiCl. Since LiCl does give an H−H stretching vibration at 4079 cm^{-1} in argon matrices containing dilute H_2,[8] we report here results obtained for mixtures of dihydrogen and LiCl in neon matrices. Matrices were formed from LiCl vapors originating from a cell that was heated from 460 to 670 °C. Features were observed in the ^{7}Li−Cl stretching region which are assigned to the monomer ion-pair at 623.2 cm^{-1} and dimer at 502 cm^{-1}. The latter is broad and is never completely absent from the spectrum. In argon, the corresponding Li−Cl stretch appears at 579 cm^{-1} and at 643 cm^{-1} in the vapor phase.[11] Although it is reasonable to expect LiCl to diffuse more readily than LiI, the dimer may arise from the gas phase as bands are seen in argon matrices in the same region with sublimation temperatures as low as 480 °C. The positions are at 491, 488, and 480 cm^{-1}. Figure 4 shows spectra taken under a variety of conditions with LiCl. Even with no dihydrogen doped into the gas mixture, there is weak intensity at 4122.7 cm^{-1} in the H−H stretching region. With this feature are others to lower wavenumber which are hardly distinguishable from noise. At higher dihydrogen concentration, these features become more apparent. Two experiments were run with 70 ppm of H_2 at 510 and 540° C. They resulted in nearly identical spectra in the region of the H−H stretch, even though the features due to dimer LiCl were much more prominent at the higher temperature. We conclude from this that LiCl aggregate species do not result in observable intensity in the H−H stretching region, similar to what we claim for LiI. As with LiI, we are not able to report a Li−Cl stretch which can be assigned to LiCl:xH_2 for any value of $x \geq 1$. As with LiI, additional features appear at lower wavenumber than 4123 cm^{-1} with increasing H_2 concentration and then at higher wavenumber with still higher concentrations. Table 1 shows the positions of principal absorptions for the H−H stretch and correlated features from HD and D_2-containing matrices.

We assign the features at 4123 and 4116 cm^{-1} to the 1:1 complex H_2:LiCl for the same reasons used in the assignment of H_2:LiI. The absorption centered at 4116 cm^{-1} is complex, certainly the contour is not as simple as the band at 4100 cm^{-1} of LiI. Using the ratio of positions observed for p-H_2:LiI and HD:LiI in neon, one predicts that there should be absorption in the HD/LiCl spectrum at 3596 cm^{-1}, corresponding to 4123 cm^{-1}. An absorption is observed at this position. Thus, as with LiI and H_2, the splitting in the diprotium spectrum is probably due to ortho-para isomers.

We have argued that dihydrogen binds at the chloride ion of LiCl in argon matrices and that this interaction results in a band at 4079 cm^{-1}. Do the bands at 4123 and 4116 cm^{-1} seen in neon result from a similar assembly? To answer this question, one must anticipate the shift which results from switching to the less polarizable neon from argon. The shift is large for some molecules. HF, for instance, is observed at 3993 cm^{-1} in neon, while it appears split at 3964 and 3954 cm^{-1} in argon. By contrast, the C− O stretch of CO shifts by 7 cm^{-1} to the red in going from neon to xenon.[12] The position of the H−H stretch is 19 cm^{-1} to smaller wavenumber in argon as compared to the position in the gas phase. It shifts another 19 cm^{-1} in going from argon to xenon matrices.[13] We presume that the shift going from argon to neon will be no larger than the shift going from argon to gas phase, or 19 cm^{-1}. What is observed is a shift of 40 cm^{-1} for H_2:LiCl in going from argon to neon. Thus, the species seen in neon is fundamentally different from the species that exists in argon. Computational modeling of H_2:LiCl in the absence of a matrix shows it to be T-shaped with no chloride interaction.[6] Were such to be the case in neon matrices, then the hydrogen is relatively free to rotate perpendicular to the Li−Cl vector and ortho-para isomers should be differentiable by infrared spectroscopy. It is less clear that there can be any easy rotation if hydrogen is bound to the halide, and we have seen nothing in argon that can be assigned to ortho-para isomerism.

KF. The alkali fluorides provide observations that shed light on the issue of matrix shifts. Ab initio calculations suggest that dihydrogen will prefer to associate with fluoride in KF.[6] The presence of argon only exacerbates this tendency. Presumably, KF:H_2 will give the same spectrum in neon as in argon. Matrices were deposited with a variety of nominal dihydrogen concentrations from 1000 to 10 ppm. The KF source temperatures ranged between 580 and 650 °C. Even when no dihydrogen had been intentionally doped in, features were observed in the region of the H−H stretch, the most prominent of which is at 4015.0 cm^{-1}. This feature corresponds to the argon position of 4014 cm^{-1} for the 1:1 complex of KF:H_2.[9] In D_2-containing matrices, the corresponding feature is especially prominent at 2878.7 cm^{-1}. These spectra and others at higher H_2 concentrations are shown in Figure 5.

In “pure” neon, a feature at 404.6 cm^{-1} is assigned to the KF stretch in the absence of interactions with H_2. The corresponding position in argon is at 396 cm^{-1}.[8] In argon this feature shifts to 382 cm^{-1} in the presence of dihydrogen, and a corresponding feature is seen in neon at 398 cm^{-1}. The intensity of the band at 398 cm^{-1} correlates with a feature at 4015.0 cm^{-1} in the H−H stretching region. These two features vanish when large quantities of dihydrogen are present. At a KF-sublimation temperature of 650 °C, a feature at 387.2 cm^{-1} is especially prominent and can be assigned to the ion-pair dimer. Moreover, on one occasion it was possible to anneal a matrix momentarily to 12 K without losing it. Growth was noted at 387 cm^{-1}, while declines occurred at 405 and 398 cm^{-1}. By using sublimation temperatures at or below 630 °C, the band at 387 cm^{-1} is much reduced or absent.

When the concentration of H_2 is greater than 70 ppm, additional features are present at larger wavenumber. They are multifaceted and cluster around 4062, 4089, and 4095 cm^{-1}. The prominence of this more complicated spectrum is dependent on the concentration of dihydrogen, with the feature centered at 4095 cm^{-1} being most prominent at concentrations of above

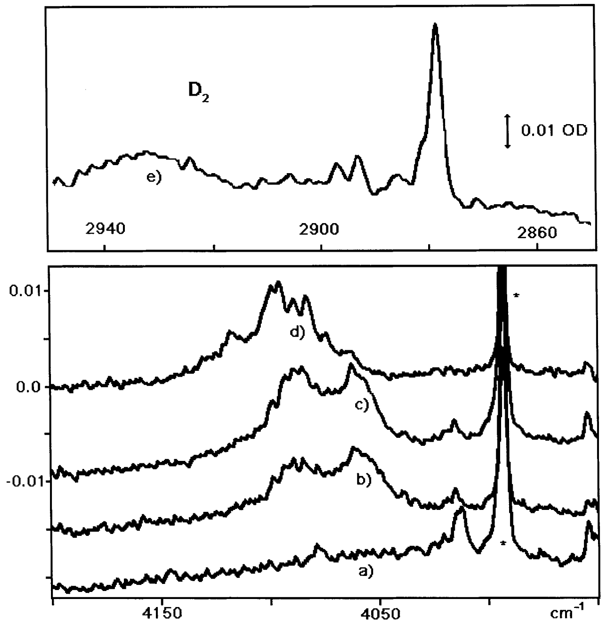

Figure 5. KF in neon matrices from sublimation source at 625 °C. Asterisk marks the position of HF. (a) No added H_2. (b) 70 ppm H_2. (c) 130 ppm H_2. (d) 660 ppm H_2. (e) 70 ppm D_2, C−H stretching features associated with pump oil have been removed by subtraction of the spectrum of a neon matrix containing only H_2 and KF.

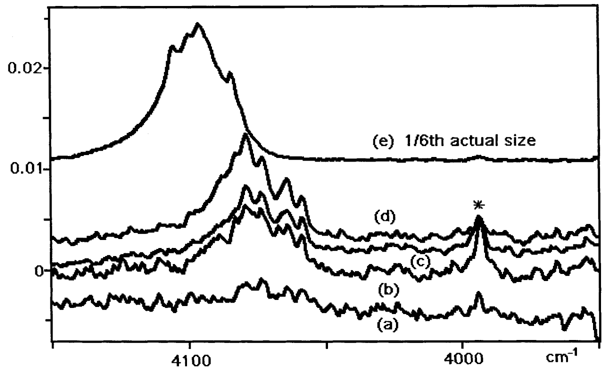

Figure 6. CsF in neon matrices. Asterisk marks the position of HF. (a) No added H_2, 610 °C source; (b) and (c) 70 ppm H_2, 580 °C source; (d) 130 ppm H_2, 580 °C source; (e) 1200 ppm H_2, 590 °C source.

650 ppm and the feature centered at 4062 cm^{-1} being dominant only at concentrations of a little more than 70 ppm. Although there are similarities between the behavior of KF in Ne/H_2 and in Ar/H_2, it is important to point out how they are different. In argon, KF$(H_2)_2$ and KF$(H_2)_3$ gave features which were easily recognized and assigned. In neon, corresponding features are not resolved from noise except for those of KF(H_2).

CsF. In argon, the spectra of CsF:xH_2 and KF:xH_2 are very similar. Finding similar spectra for KF:H_2 in both argon and neon, we next look for similarities between CsF:xH_2 and KF:xH_2 in neon. As can be clearly seen in Figure 6, the two alkali fluorides behave quite differently in neon. Matrices were formed with dihydrogen concentrations that ranged from 0 to 12 000 ppm with many experiments with concentrations at 70 ppm or below. CsF was evaporated from an effusion source that ranged in temperature from 520 to 610 °C. A peak at 336 cm^{-1} is assigned to the Cs−F stretching vibration. It corresponds to an argon and gas-phase frequency of 314 and 353 cm^{-1}, respectively.[8,11] A second band at 333 cm^{-1} appears to also be the Cs−F stretch in a different site; its behavior was not that of an adduct of dihydrogen. A peak at 264 cm^{-1} behaved as if it belongs to a dimer ion-pair, it appeared only at highest source temperatures. A broad peak is observed in the H−H stretching region which often has a structure which is hardly differentiated from noise. Still the features are repeated in numerous experiments, suggesting that the broad feature is an envelope of more narrow features. The position of maximum absorbance moves to higher frequencies at higher concentrations of dihydrogen. Again, there is an interplay between the temperature of the effusion source and the dihydrogen concentration. Features that are observed at low dihydrogen concentration may be observed at higher concentration if the concentration of the ion-pair is greater. Although there is a suggestion of absorption in the region of 4020 cm^{-1} where CsF absorbs in argon, we could not obtain these features reproducibly nor could we find conditions that would yield an adequate signal-to-noise ratio.

An Overview. There are two conclusions that can be drawn from the data. First, the frequency shifts for H_2 interacting with cations are typically less than dihydrogen interacting with anions. Second, the amount of red-shift cannot be used to infer the enthalpy of formation of the complex within the matrix.

We have argued that the species seen in neon are fundamentally different from what is observed in argon because the amount of shift in the spectrum of CsF:H_2, LiCl:H_2, and LiI:H_2 is greater than what can be attributed to changes in the polarizability of the matrix. If one accepts that dihydrogen interacts with the halide ion of MX in argon, then a substantial shift in the spectrum suggests that some amount of cation interaction either replaces the anion interaction or augments it. This is reasonable because the cations should not be so strongly solvated by neon as by argon. Thus, we can claim that the higher frequencies seen in neon can be associated with assemblies with some cation interaction.

It is interesting to note also that the features seen for LiCl and LiI move to the red when conditions favor multiple associations with dihydrogen. Only at much higher dihydrogen concentrations do features appear to the blue of the 1:1 complex. In argon, the opposite behavior is noted. As an alkali halide interacts with more than one molecule of hydrogen, new features appear at larger wavenumber.

Next, we defend the proposition that one cannot infer the energy of the interaction from the position of the infrared absorption. The neon matrices gave no evidence of extensive light scattering, and we believe them to be well-annealed. We presume that the dihydrogen is able to optimize its position vis-à-vis the ion-pair because the spectrum lacks absorptions at 4022 and 4079 cm^{-1} for H_2 complexes of CsF and LiCl, respectively. If the dihydrogen were to be frozen into position at the point of its first contact with the ion-pair, then these frequencies would be present along with others. With this evidence for rearrangement in the H_2:MX assembly, we assert that the species which are seen in neon represent the most stable assemblies of H_2, Ne, and an isolated ion-pair. If the red-shift of the infrared spectrum were a measure of the strength of the interaction, then one would expect LiCl to produce the band at 4079 cm^{-1} in neon that is seen in argon because, according to the assumption, this species must be most stable. However, species giving absorptions at 4123 and 4116 cm^{-1} are observed and we have argued that they belong to the most stable species. Thus, for these weakly interacting systems, the position of the H−H stretch cannot infer relative stability. Conceivably, for complexes of identical structure there will be a correlation between stability and frequency, but there is no way of ascertaining whether structures are identical.

It came as a surprise that we were not able to obtain a complex of CsF and H_2 in neon that resembled what was seen in argon analogous to what is seen for KF. If the interaction between rare gas and cation scales as the charge-to-radius ratio, then solvation of the cation will be greater for potassium, even in neon. Lacking such strong interactions with cesium, the dihydrogen may effectively compete for sites in close proximity to cesium, even as it interacts with the fluoride. Neon may shut out dihydrogen from getting close to that cation in KF, at least for the 1:1 complex. With larger numbers of H_2 in association with KF, the likelihood of potassium−dihydrogen interactions increases despite the neon.

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References and Notes

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