Infrared Characterization of Simple Adducts of Matrix-Isolated Cesium Fluoride and Sodium Chloride with Dihydrogen: Evidence of a Cation Interaction

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H_2-doped argon matrices containing CsF were examined using FTIR with 1 cm^{-1} spectral resolution. Several distinct trapping sites were identified with one, two, and three hydrogen molecules perturbed by CsF. CsF(H_2) gives a band at 4022 cm^{-1} while the features of CsF$(H_2)_x$, $x > 1$, are displaced to higher wavenumbers. It is clear from the similarity of the spectra of H_2 and HD that the rotation of H_2 is quenched in the presence of CsF. Analogous spectra are observed using KF with the 1:1 adduct absorbing at 4016 cm^{-1}. The spectrum of H_2 in argon matrices doped with NaCl shows three absorptions that exhibit fine structure even under highly dilute conditions. Analogous features are exhibited by HD, indicating that the several bands are probably not due to rotation of the hydrogen. The three bands are assigned to conformers of NaCl:H_2 which are differentiated by an interaction between the sodium ion and H_2 that is modulated by the matrix.

Recently, we reported that alkali halides perturb dihydrogen, thus making the H−H stretch readily observable in argon matrices.[2] The position of the H−H stretch is shifted to smaller wavenumber, the extent of which is greatest for the alkali halide with the smallest anion and is nearly independent of the size of the cation. This led us to claim that the anion was responsible for the perturbation. It was apparent that either the cation was incapable of inducing in H_2 an easily observed infrared spectrum or hydrogen was excluded from close proximity with the cation by the argon.[3] The results of that study threw into question the presumption that the H−H stretch observed in zeolites is due to hydrogen associated with cation sites,[4] although recent work supports the view that oxygen may also be involved.[5,6] In the earlier study, it was not possible to observe dilute matrices at high resolution because of equipment limitations.[2] Herein we report the results of high-resolution experiments using H_2, HD, and D_2 in which we characterize several associations of dihydrogen and CsF and related experiments with NaCl and RbCl. In the earlier study, sodium chloride was anomalous among the alkali chlorides. Whereas the other alkali chlorides produced a perturbed H−H stretch at 4078 ± 3 cm^{-1}, NaCl produced a complex feature at 4104 cm^{-1}. The anomalous behavior can now be understood as resulting from a mixture of conformers which involve, to some degree, interactions with the cation.

Experimental Section

Matrices were deposited at 10 K on a CsF window in a fashion similar to that reported earlier.[2] NaCl (Mallinckrodt) and KF(MCB) were analytical reagent grade. RbCl (Sargent) was listed as chemically pure, and CsF (Aldrich) was 99.9% pure. All were used without further purification. The alkali halides were loaded into a quartz ampule, the end of which was constricted to a diameter of approximately 2 mm. The ampule was placed approximately 15 cm from the Displex cold end in an 18 mm Vycor tube; its temperature was monitored by a thermocouple. The Vycor tube was heated by a resistance wire that was wound so that the alkali halide would be sublimed in a cooler region of the tube and heated still hotter before it exited the tube, approximately 6 cm from the cold end.

Argon (99.999% pure) and H_2 (99.9% pure) were obtained from Lincoln Big Three and passed through tubes of Ascarite and molecular sieves before use. Kr (99.995% pure), Xe (99.995% pure), and D_2 (99.9% pure) were obtained from Air Products, and HD (99% pure) was obtained from MSD Isotope. They were used without further purification.

Spectra were recorded with 1 cm^{-1} resolution by using a Perkin-Elmer Model 2000 FTIR equipped with a CsI beam splitter. Attempts at obtaining FT Raman spectra of the D-D stretch perturbed by CsF and RbCl were made without success; only unperturbed D_2 was observed.

Results and Discussion

CsF(H_2). CsF was deposited at high dilution in argon matrices doped with hydrogen the concentrations of which ranged from 0.6 to 12 mol %; representative spectra are shown in Figure 1 in the region of the H−H stretch. A prominent band is observed at 4022 cm^{-1} when the hydrogen is most dilute. This band is accompanied by two others at 4026 and 4030 cm^{-1}, which become more prominent at higher hydrogen concentrations while other bands become more important at still higher concentrations. With 0.6% hydrogen present, there is a single sharp band at 313.6 cm^{-1}, which is assigned to CsF in pure argon, accompanied by a broader band at 310 cm^{-1}.[7] As hydrogen becomes more concentrated, these bands are replaced by a broad feature centered at 303 cm^{-1}.[8] If one presumes

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(2) Ogden, J. S.; Rest, A. J.; Sweany, R. L. *J. Phys. Chem.* **1995**, *99*, 8485.

(3) An interaction between Ar and the beryllium of BeO may be as strong as 7 kcal/mol. Frencking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007. Thompson, C. A.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 423.

(4) Larin, A. V.; Cohen De Lara, E. *J. Chem. Phys.* **1994**, *101*, 8130 and literature cited therein.

(5) Bordiga, S.; Garrone, E.; Lamberti, C.; Zecchina, A.; Areán, C. O.; Kazansky, V. B.; Kustov, L. M. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3367.

(6) Wakabayashi, F.; Fujino, T.; Kondo, J. N.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1995**, *99*, 14805.

(7) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

(8) The position of the Cs−F stretch is dependent on the mass of the hydrogen.[2]

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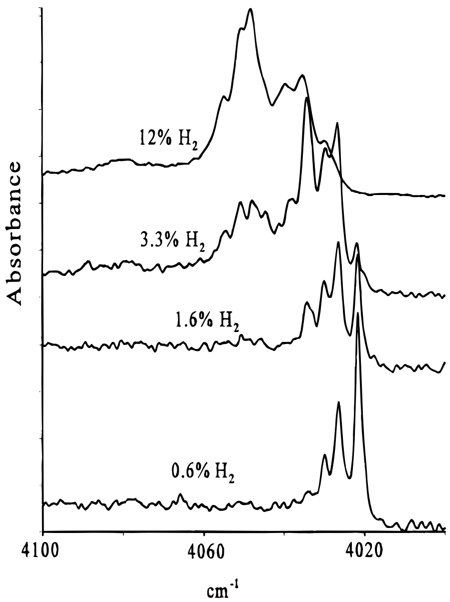

Figure 1. Spectra in the HpH stretching region of H_2 in association with dilute CsF as a function of the H_2 concentration.

that a single dihydrogen in the vicinity of a CsF ion pair causes a shift in the position of the Cs−F stretch, then a fraction of the CsF ion pairs are isolated in pure argon cages when the H_2 is most dilute. The next most likely environment is a cage containing a single H_2 molecule. Thus, the band at 4022 cm^{-1} is assigned to $CsF(H_2)$. Consistent with such an assignment, mixtures of dilute H_2 and D_2 continue to give good intensity at 4022 cm^{-1} and at 2889 cm^{-1}, its corresponding position in the D_2 spectrum.

$CsF(H_2)_2$. The bands at 4026 and 4030 cm^{-1} are assigned to $CsF(H_2)_2$, the two being the symmetric and antisymmetric combinations of the H−H stretching modes. When a mixture of equal parts of D_2 and H_2 was deposited at high dilution with CsF, a single band at 2893.0 cm^{-1} assigned to $CsF(H_2)(D_2)$ almost replaces the bands at 2894.9 and 2892.1 cm^{-1} of $CsF(D_2)_2$. The spectrum in the region of the H−H stretch is not nearly so perturbed, there being a shoulder at 4028.5 cm^{-1}. With due regard to mobility, the probabilities of the various isotopic molecules, $CsF(D_2)_2$, $CsF(H_2)(D_2)$, and $CsF(H_2)_2$, ought to increase as the proportion of diprotium in the formula unit increases. Thus, it is expected that the spectrum of $CsF(H_2)(D_2)$ ought to dominate the spectrum of $CsF(D_2)_2$ in the region of the D−D stretch, whereas the spectrum of $CsF(H_2)_2$ ought to dominate that of $CsF(H_2)(D_2)$ in the region of the H−H stretch.

The intensities of the two bands of $CsF(H_2)_2$ provide structural information. One can calculate the angle between the two oscillating hydrogen molecules by using intensities if one assumes that the H−H stretch is an isolated mode, analogous to how carbonyl modes are used to calculate bond angles in metal carbonyls.[9] If the band at 4030 cm^{-1} is the in-phase combination, then the angle between the hydrogen molecules is 121° ± 3°, where the uncertainty is derived from the uncertainty in the ratio of areas. If the out-of-phase combination is the high-frequency mode, then the angle is computed to be 62° ± 6°. The interactions between Ar and $CsF(H_2)_2$ are probably significant.[10] Thus, it is not clear that the structure of $CsF(H_2)_2$ in argon will be the same as what might be the case for truly isolated $CsF(H_2)_2$.

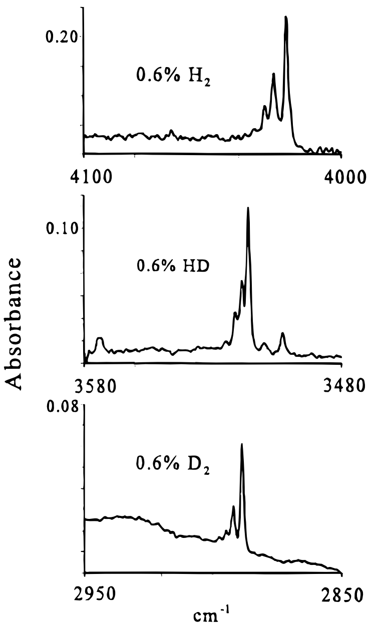

Figure 2. Spectra of H_2, HD, and D_2 at high dilution with CsF in Ar.

Table 1. Positions of the H−H stretch in Ar matrices[a]

x	$CsF(H_2)_x$	$CsF(HD)_x$	$CsF(D_2)_x$	$KF(H_2)_x$	$KF(D_2)_x$
1	4022	3516	2889	4014	2882
2	4026	3519	2892	4022	2889
	4030	3522	2895	4026	2892
3	4034	3525[b]	2897	4029	2894

[a] Positions in cm^{-1} are ±1.0 cm^{-1} when bands are well-resolved. Positions are dependent also on the mixing ratio of H_2 in argon. [b] Spectrum only observed at high dilution, making the assignment of this small absorbance more tenuous.

$CsF(H_2)_x$, $x > 2$. At still higher H_2 concentrations, one expects features of $CsF(H_2)_3$ to become more prominent. The single band at 4034 cm^{-1} is assigned to this species. Other bands appear at still higher wavenumbers, but none of them could be assigned to $CsF(H_2)_3$ with certainty. At yet higher H_2 concentrations, absorptions are found at still higher wavenumbers. As in the earlier study, the features assigned to $CsF(H_2)_x$, $x \leq 3$, appear at nearly the same positions in spectra of hydrogen in KF-doped argon matrices. The absence of a significant cation influence on the positions leads us to conclude that the hydrogen that gives these features does not interact with the cation. However, as the number of H_2 molecules around the fluoride ion increases, it becomes increasingly probable that the hydrogen will be influenced by the cation. The features at 4050 cm^{-1} may be analogous to those seen in the spectrum of NaCl (vide infra).

$CsF(HD)_x$ and $CsF(D_2)_x$, $x \geq 1$. The spectra of HD and D_2 are analogous to that of H_2 in the presence of CsF. Figure 2 shows the relevant regions of the spectrum, and Table 1 contains the positions for the various species. It was shown previously that the anions of alkali halide ion pairs perturb the H−H stretch of H_2 in argon matrices.[2] It was unclear whether the rotation of hydrogen was quenched by the interaction. The similarity of the spectrum of H_2 with that of HD suggests that *o*-H_2 and *p*-H_2 are indistinguishable or that one of the isomers is infrared silent. *p*-H_2 is infrared silent in solid hydrogen[11] and in associations with weaker Lewis bases[12] and could conceivably be infrared silent in these experiments. The ease with which

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(9) Burdett, J. K. *Inorg. Chem.* **1981**, *20*, 2607.

(10) Gush, H. P.; Hare, W. F. J.; Allin, E. J.; Welsh, H. L. *Can. J. Phys.* **1960**, *38*, 176.

(11) See ref 3. As further evidence of a significant interaction with the matrix itself, the position of the H−H stretch of $CsF(H_2)$ in Kr is 4009.6 cm^{-1}, a 12 cm^{-1} red shift from the position in Ar.

HD is observed and the similarity of the HD spectrum to that of H_2 suggest that HD in the ground rotational state is infrared active in the presence of CsF, implying that p-H_2 is infrared active also. Analogous arguments can be made for both RbCl and NaCl on the basis of similarities of the spectra of HD and H_2. We conclude that the rotation of hydrogen is quenched in its association with NaCl, RbCl, and CsF. The alternative explanation that o-H_2 is infrared silent is less credible.

A reviewer has wondered whether the nuclear spin relaxes rapidly in the presence of the ion pairs. Rapid nuclear spin conversion requires an oscillating magnetic field and has been observed in the presence of dioxygen.[13] The pure rotational transition of o-H_2 that is not perturbed by the alkali halide is observed in the matrices throughout the experiments. Thus, there are no paramagnetic impurities in the bulk matrix that cause relaxation. For that hydrogen that is perturbed by alkali halide, to observe only perturbed p-H_2, the ion pair, itself, would have to cause the relaxation of o-H_2. Moreover, if the relaxation occurs, it must occur in a very short time interval because the intensity pattern does not change between successive spectra made as close as 5 min apart. Alkali halide surfaces are not thought to induce ortho−para spin conversion, and it is unreasonable to expect the ion pair to behave differently.[14] Thus, it more likely that the rotation of H_2 is quenched.

The polarizability of H_2 is anisotropic. At a 403 pm separation between H_2 and CsF, hydrogen is 48 J mol^{-1} more stable in the parallel orientation than in the perpendicular orientation.[15] At 10 K, this barrier by itself is insufficiently large to quench the rotation of H_2. For the rotation to be quenched, the argon must be a non-neglible contributor to the barrier.

RbCl. The spectra obtained at high resolution resemble those reported previously.[2] A single band at 4073.4 cm^{-1} (FWHM 5.5 cm^{-1}) was observed with 1% H_2 in argon. With 13% H_2, a band is observed at 4077.4 cm^{-1} (FWHM 6.0 cm^{-1}). Neither band is completely symmetrical, but there is otherwise no evidence of the fine structure that was observed with CsF. The shift to higher wavenumber is analogous to the behavior of CsF-$(H_2)_x$ where the positions of the absorptions move to higher wavenumbers as x is increased. Two bands are observed at higher wavenumbers at 4100 and 4106 cm^{-1} in the region where an absorption was observed at low resolution.[2] This band was previously assigned to aggregate RbCl and hydrogen; nothing in these subsequent experiments overturns that assignment although there may be contributions from RbCl:H_2 interactions that involve a contribution from the cation (vide infra). The position of the D−D stretch is 2927.1 cm^{-1} in 3% D_2, and the position of the H−D stretch is 3556 cm^{-1}. A small shoulder is observed at 3552 cm^{-1}.

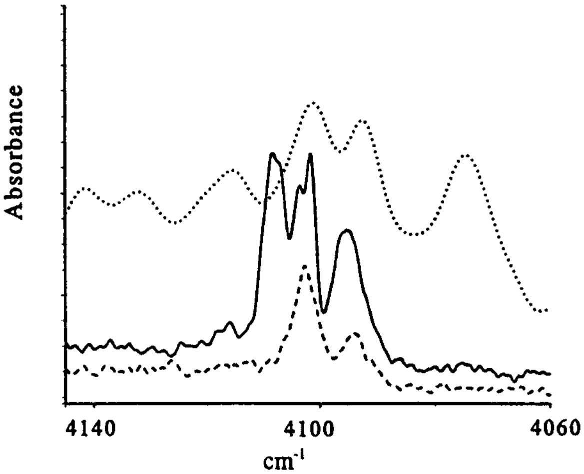

Figure 3. Solid line: spectrum of 0.6 mol % H_2 in NaCl/Ar. Dashed line: spectrum of 1.8 mol % H_2 in NaCl/Kr. Dotted line: the spectrum of 2.0 mol % H_2 in NaCl/Xe. The latter spectrum was the average of two matrices, grossly affected by scattering. The spectrum has been smoothed.

Table 2. Positions[a] of Absorptions of Dihydrogen in NaCl-Containing Matrices

Ar			Kr	Xe	
H_2	HD	D_2	H_2	H_2	D_2
4116.2[b]					
4110.8	3579.2 sh	2955.3			
4108.5	3580.8	2952.9			
4106.6					
4103.5	3584.0 sh	2950.5	4102.6	4101.4	2948 br
4101.7	3586.3	2948.7			
4094.5	3579.2 sh	2945.4	4094.1	4092.3	
	3580.8	2944.0			
		2940.5 sh			
		2930.7[c]		4074.5[c]	2927.4[c]

[a] Positions are in wavenumbers and are ±1.0 cm^{-1} when bands are well-resolved. Positions vary with mixing ratio of H_2 in argon. [b] Absorption noted when NaCl is relatively concentrated, assigned to aggregate features. [c] Position noted for the H-H stretch for other alkali chlorides.

NaCl. The spectrum of H_2 perturbed by NaCl is complex even when the concentration of H_2 is very dilute and the concentrations of NaCl aggregates are also low. Thus, the spectra shown in Figure 3 are probably those of NaCl(H_2). Table 2 gives the positions of maximum absorbance. The spectrum in argon is characterized by three clusters of bands. The complex at 4108 cm^{-1} is not observed in Kr nor in Xe. The positions of the other two complex bands are red-shifted by 2 cm^{-1}. These two bands are also seen in Xe, along with a band at 4074 cm^{-1} which is the position observed for the H−H stretch perturbed by all the other alkali chlorides.[2] The Xe matrices were highly scattering, and the signal-to-noise ratio was low as a result. The feature shown in Figure 3 at 4074 cm^{-1} is corroborated by the observation of an analogous absorption at 2928 cm^{-1} for D_2 with better signal-to-noise discrimination. A weak band at 2931 cm^{-1} is also observed in argon as shown in Figure 4.

The relative intensities of the complex bands due to H_2 in argon are altered by annealing. The complex bands at 4108 and 4102 cm^{-1} are attenuated while the band at 4095 cm^{-1} becomes more intense as the temperature is raised to 23 K. The changes are not reversed as the temperature is lowered to 10 K. Above 23 K, even the intensity of the band at 4095 cm^{-1} is attenuated.

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(12) Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *J. Phys. Chem.* **1990**, *94*, 1352.

(13) Prochaska, F. T.; Andrews, L. *J. Chem. Phys.* **1977**, *67*, 1139.

(14) Dai, D. J.; Ewing, G. E. *J. Chem. Phys.* **1993**, *98*, 5050.

(15) The polarizability of H_2 is 0.345×10^{-40} m^3 greater in the parallel orientation than in the perpendicular orientation.[16] Thus, there will be a stronger interaction, ΔV, in the parallel direction given by

$$\Delta V = -2\mu^2(\alpha_{\|} - \alpha_{\perp})/(16\Pi^2\epsilon_0 R^6)$$

where ϵ_0 is the permittivity of vacuum, μ is the dipole moment of CsF, and α is the polarizability in the parallel and perpendicular orientations. Our estimate of R was obtained by using the van der Waals and covalent radii of H_2, the ionic radius of fluoride, and the Cs−F bond length;[17] the dipole moment of CsF is 7.85 D.[18]

(16) Gough, K. M.; Yacowar, M. M.; Cleve, R. H.; Dwyer, J. R. *Can. J. Chem.* **1996**, *74*, 1139. Kolor, W.; Wolniewicz, L. *J. Chem. Phys.* **1967**, *46*, 1426.

(17) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry; Principles of Structure and Reactivity*; Harper Collins College Publishers: New York, 1993.

(18) Davis, S. L. *J. Chem. Phys.* **1988**, *88*, 1080.

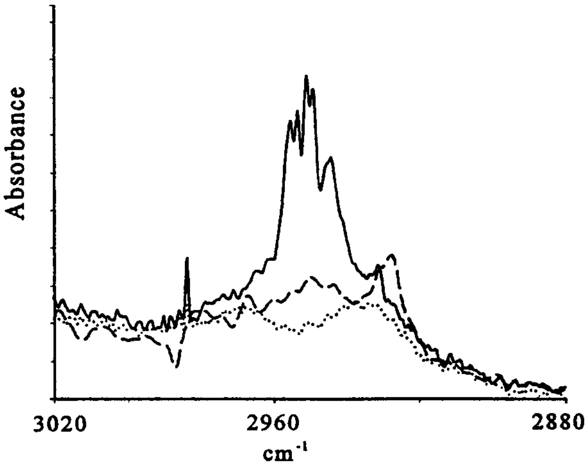

Figure 4. Spectrum of D_2 induced by NaCl in Ar and Xe matrices. Dotted line: spectrum of background in the region. Dashed line: spectrum of 8 mol % D_2 in NaCl/Xe. Solid line: spectrum of 1.2 mol % D_2 in NaCl/Ar.

NaCl represents a special case in the series of alkali chlorides in not inducing a feature at 4078 cm^{-1} in the spectrum of H_2 in argon.[2] It was surprising, therefore, to observe this feature for H_2 in Xe and also the corresponding feature with D_2 in argon. The species resulting in an absorption at 4074 cm^{-1} must not be the thermodynamically most favored species. The observation of this species must depend on subtle environmental factors and on the quenching rate of the matrix. The most stable isomer of $NaCl(H_2)$ must be that which absorbs at 4094 cm^{-1}. If the species which exhibits an H−H stretch at 4074 cm^{-1} has no $H_2{-}Na^+$ interactions, then either the species absorbing at 4094 cm^{-1} does have $H_2{-}Na^+$ interactions or the argon cage itself perturbs the spectrum by 20 cm^{-1}. This latter possibility seems unlikely given the fact that the position of the band at 4094 cm^{-1} is so little altered by changing rare gas atoms from argon to xenon. The rare gas atom may indeed enforce a structure on the aggregate $NaCl{:}H_2$, but the frequency shift of the hydrogen is due to the extent of interaction with the sodium and chloride ions.

To summarize our view of the system $NaCl/H_2/Ar$, the band at 4074 cm^{-1} is due to a species with an end-on association between H_2 and the chloride ion of NaCl. The band at 4094 cm^{-1} and those at higher wavenumbers are due to $NaCl(H_2)$ with some interaction between the sodium ion and H_2 while some contact with the chloride ion is still maintained. The multitude of infrared absorptions is due to the system not being able to achieve its most stable conformation during the period of quenching as the matrix is deposited.

This behavior having been noted, it is interesting to compare the behavior of H_2 in matrices and H_2 on NaCl surfaces. H_2 adsorbed on surfaces gives features at 4110 and 4133 cm^{-1} which are assigned to p-H_2.[14] Additional features are seen at 4100 and 4122 cm^{-1} which are assigned to o-H_2. The bands at 4100 and 4110 cm^{-1} are ascribed to H_2 that has been adsorbed on defect sites whereas the bands at 4122 and 4133 cm^{-1} are assigned to H_2 on a smooth-face surface. The band ascribed to a defect site is nearly coincident with the position of a matrix band which is assigned to $(NaCl)_xH_2$ where x is most likely 2. The fact that H_2 is presumed to rotate on this defect site of the surface whereas H_2 does not rotate in the matrix reflects the lower temperature of the measurement and the more complex potential for H_2 in a matrix where terms involving interactions with NaCl and rare gas atoms must be included. It is interesting to note that the hydrogen has been presumed to be associated with the cation site of the surface,[14,19,20] although spectra of HD on NaCl surfaces have given evidence of still another site in which the chloride ion has been presumed to play a role in the binding.[21] The position of this absorption is 10 cm^{-1} to the blue of the band ascribed to H_2 adsorbed on smooth-surface sites. In light of the present study, it may be that the anion is involved in all infrared observations involving surfaces (vide infra).

The currently prevalent idea that H_2 interacts primarily with cation sites also colors the interpretation of the spectrum of H_2 in zeolites. However, in an extensive study, Bordiga et al. have observed the spectrum of H_2 adsorbed in a variety of zeolites and have shown that the extent of perturbation is greatest for those materials with the highest Al:Si ratio.[5] This has led them to conclude that there is an interaction with the oxide of the framework concomitant with an interaction with an acidic site. The frequencies observed in this study range from 4075 to 4150 cm^{-1}. A similar interpretation was offered by Wakabayashi et al.[6] The assignment of the lowest wavenumber to the adduct with an involvement of the anion goes counter to the assignment of the feature arising from HD adsorbed on NaCl surfaces cited in the previous paragraph. The conclusions of this study also support the view that the shift resulting from an anion can be more extreme than what will be observed when cation interactions are admixed.

If the system $NaCl/H_2/Ar$ is understood, then one might wonder why we have assigned no specific features to H_2 under the influence of the Cs^+ in the system $CsF/H_2/Ar$. However, when CsF is deposited at temperatures higher than 10 K and with higher H_2 concentrations, features are observed in the region of 4050 cm^{-1} which had been previously identified as aggregates.[2] These features probably also derive intensity from H_2 which is associated in some fashion with the cation. Once three H_2 molecules populate the cage of a fluoride ion, then additional H_2 must be oriented in such a fashion as to allow an interaction with the cesium ion even if there continues to be an end-on interaction with the fluoride. Evidence that the fluoride is still involved to some extent with the H_2 that gives rise to the complex band at 4050 cm^{-1} is proven by the lack of any intensity in the region of 4050 cm^{-1} for CsCl, CsBr, and CsI, even when H_2 is concentrated.

Thus, one can conclude from these experiments that hydrogen under the influence of only the anion of these two salts gives the largest red shift of the H−H stretch. It also seems clear that the anion is involved with H_2 in nearly all features that have been observed. As the anion interaction is augmented by cation interactions, then features with less extreme red shifts are observed.

Dedication. We note that Professor Jack Halpern characterized base interactions with H_2 in the 1950s. We dedicate this paper in his honor on the occasion of his retirement.

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(19) Olman, M.; Kozirovski, Y. *J. Colloid Interface Sci.* **1972**, *38*, 51.

(20) Heidberg, J.; Dierkes, W.; Schönekäs, O.; Schwarte, R. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 131.

(21) Dai, D. J.; Ewing, G. E. *J. Chem. Phys.* **1994**, *100*, 8432.