

# Infrared Spectra of Argon Matrix-Isolated Alkali Halide Salt/Water Complexes

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**Abstract:** The reaction products of alkali halide salt molecules with H<sub>2</sub>O and its isotopic counterparts at high dilution in argon matrices have been investigated. The infrared spectra of these complexes show two bands in the O-H stretching region, and two bands between 400 and 700 cm<sup>-1</sup>, which show a slight dependence on both the alkali metal cation and the halide anion. These results have been interpreted to indicate that a pyramidal structure is formed in which the metal cation is bound to the oxygen of the water molecule, and that the anion sits as a counterion at the base of the pyramid and interacts through hydrogen bonds to the water molecule. The two low-frequency vibrations show a strong hydrogen dependence and are assigned to the two hydrogen deformation modes anticipated for a C<sub>s</sub> pyramidal structure. The infrared spectra of transition metal aquo complexes, used as a model for these complexes, support the assignment of a metal cation-bound species. Comparison of these results to the theoretical calculations on such complexes is made as well.

## Introduction

The interactions of alkali metal cations with water and other bases have generated extensive interest over the years, from the biological implications in nerve axons to the solution studies of strong electrolytes.<sup>1-4</sup> Numerous efforts have been made in the past few years to sort out the different aspects of these interactions, and in particular when competitive hydration of both an alkali metal cation and a halide anion can occur. Kebarle and co-workers have thoroughly investigated the gas-phase hydration of both alkali metal cations and halide anions, and determined heats of hydration for one to six water molecules.<sup>5,6</sup> While the heats of hydration for several H<sub>2</sub>O molecules are more directed toward concentrated aqueous solution, the data for hydration of a single alkali metal cation, or halide anion, are of interest for competitive hydration in an isolated environment, either gas phase or inert matrix. Recently, Devlin and co-workers have looked at the low-temperature spectra of small amounts of water in M<sup>+</sup>ClO<sub>4</sub><sup>-</sup> glasses, to determine the relative effects of hydrogen bonding to the water and interactions of the metal cations with the water molecules.<sup>7</sup> These workers have also studied the cation-water interaction through the infrared spectra of alkali nitrate and chlorate ion pairs in glassy H<sub>2</sub>O matrices. Devlin and co-workers have also investigated argon-matrix-isolated samples of alkali metal nitrates and H<sub>2</sub>O, over the range 6 to 100% H<sub>2</sub>O, focusing their studies on the nitrate anion bands to determine the hydration effects of the water molecules.<sup>9</sup> These studies were then related to vibrational spectra of these same alkali metal nitrates in dilute aqueous solution, which have been the subject of numerous investigations over the years.<sup>10</sup>

Numerous theoretical calculations have been directed toward elucidation of the M<sup>+</sup>·H<sub>2</sub>O complex, from very simple models to detailed ab initio calculations.<sup>11-14</sup> The most sophisticated of the calculations have been able to reproduce well the experimental heats of hydration in the gas phase, as well as the geometry of the complex, and one calculation predicts vibrational frequencies of the complex.<sup>12</sup>

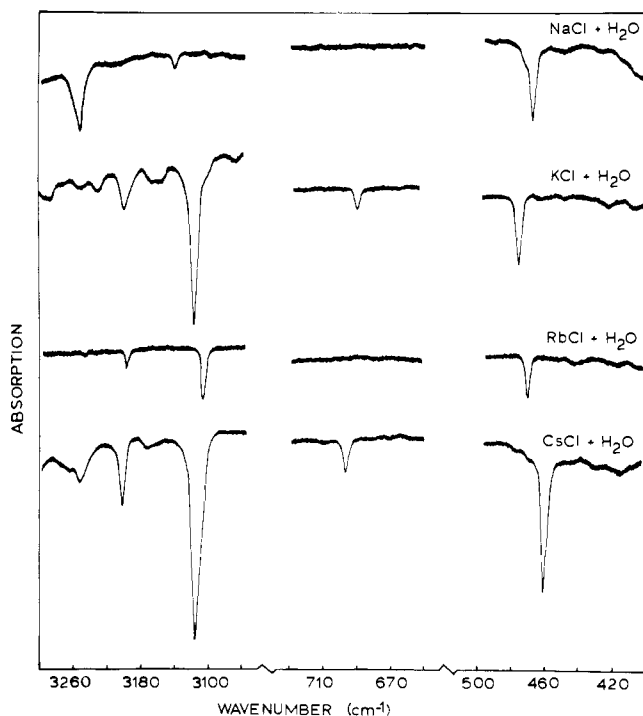
With the obvious interest in these interactions, from both experimental and theoretical points of view, a study of the matrix isolated complex is suggested. The salt-molecule reaction technique has been used in argon matrices to transfer the halide anion of an alkali halide salt molecule to a Lewis acid, to form an anion of interest in an ion pair.<sup>15-17</sup> Similarly, reactions of these salt molecules with Lewis bases and, in particular, with H<sub>2</sub>O might lead to a complex in which the alkali metal cation has transferred to the base to form a

M<sup>+</sup>·H<sub>2</sub>O complex in an ion pair. Of course, under these circumstances, a hydrogen bonding interaction can also occur, which might represent the competition between the alkali metal cation and the halide anion for the H<sub>2</sub>O in an isolated ion pair. With all of the theoretical results available, this complex will also provide a comparison of experiment and theory, so a complete study of the interaction of alkali halide salt molecules with H<sub>2</sub>O was undertaken, with systematic variation of both the alkali metal cation and the halide anion. (Reactions of the alkali fluoride salts with H<sub>2</sub>O have not been considered in the present work—the unique reactivity of the fluoride anion leads to very different spectra than those presented here and will be reported at a later date.)

## Experimental Section

All of the experiments conducted for this study were carried out in a completely stainless steel vacuum system, with Nupro Teflon-seat valves. Pumping was provided by a Model 1402B Welch vacuum pump, and a Varian M-2 diffusion pump, with liquid nitrogen trap. Vacuums near 10<sup>-7</sup> mm at the gauge (cold cathode, Varian) were generally recorded at the start of an experiment. Cryogenics were supplied by a Model 21 closed cycle refrigerator (CTi, Inc.), operating down to 10 K. However, normal temperatures during deposition ranged near 14–16 K. Gas samples were deposited from 2-L stainless steel vessels through a finely metering valve onto the cold surface, a CsI window mounted with indium gaskets to the copper cold block. Deposition of the gas samples was essentially perpendicular to the cold surface. Temperatures at the cold surface were measured with a gold-doped cobalt vs. iron thermocouple, and window temperatures were regulated by supplying a constant voltage to two 10-W button heaters mounted near the cold window. The alkali halide salts were heated and vaporized in a small resistively heated oven employing chromel A heating wire, and deposited at approximately a 45° angle to the cold surface. The vacuum vessel was equipped with CsI windows throughout, and sat in the sample beam of a Beckman IR-12 infrared spectrophotometer for the duration of the experiment, to allow monitoring of the sample during deposition.

Triply distilled H<sub>2</sub>O was used for experiments employing normal isotopic H<sub>2</sub>O. A small amount, 1–2 mL, was put into a glass finger and repetitively frozen, pumped on, thawed, and pumped for several freeze/thaw cycles to remove any volatile species. For deuterated experiments, D<sub>2</sub>O (99.8%, Merck) was employed with a similar number of freeze/thaw cycles. To guard against isotopic exchange during the experiment, the entire vacuum manifold was conditioned with D<sub>2</sub>O vapor before preparation of the actual experimental sample. D/H ratios of at least 6 were easily obtained in this manner. In several experiments, <sup>18</sup>O-enriched H<sub>2</sub>O was employed (95%, Merck), with the usual freeze/thaw cycles. The salts employed were NaCl (Mallinckrodt, analytical reagent), KCl (Allied, reagent), RbCl (Fairmount), CsCl (Fisher), CsBr (Orion), CsI (Harshaw), and KCN



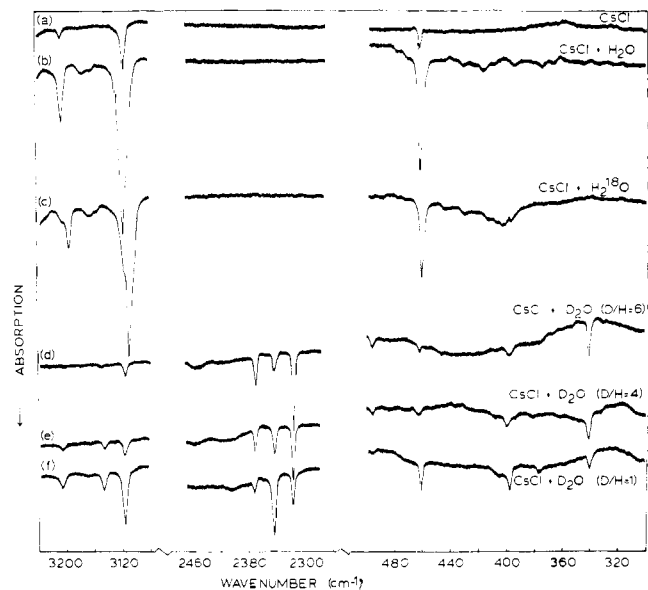
**Figure 1.** Infrared spectra of each of the alkali chloride salts deposited into an Ar matrix containing H<sub>2</sub>O at M/R = 600, over the spectral regions 400–500, 650–730, and 3060–3280 cm<sup>-1</sup>, after 20–24 h deposition at 14 K.

(Fisher). Argon and nitrogen were used as matrix gases without further purification.

Gas samples, with matrix/reagent ratios (M/R) from 500 to 2000, were deposited at a rate of 2 mM/h for 24–36 h before final spectra were recorded. The salts were outgassed in the oven, behind a closed door, for several hours before an experiment, at temperatures exceeding those used during the experiment. The deposition temperatures for these salts were NaCl, 600 °C; KCl, 550 °C; RbCl, 525 °C; CsCl, 500 °C; CsBr, 500 °C; CsI, 500 °C; and KCN, 550 °C, although a range of temperatures around these indicated were used to provide a range of concentrations in the matrix. Infrared scans were taken intermittently during the experiment, with final scans after deposition was finished. Final scans consisted of a survey scan from 4000 to 200 cm<sup>-1</sup>, followed by high-resolution scans at expanded scale, of all regions of interest. In many cases, the matrices were then slowly warmed to about 40–44 K to allow diffusion, and then recooled to 16 K and rescanned.

## Results

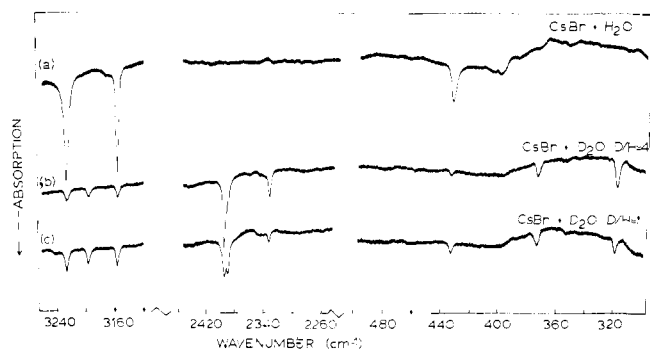
Before the spectra of the reaction products of the alkali halide salts with H<sub>2</sub>O were recorded, the spectra of the H<sub>2</sub>O or isotopic molecules in Ar alone were recorded carefully. Since H<sub>2</sub>O has been demonstrated to rotate in an Ar matrix,<sup>18–20</sup> a number of bands were observed in these experiments near the three fundamentals of H<sub>2</sub>O. When a sample of Ar/H<sub>2</sub>O = 600 was deposited, the spectra revealed bands at 3578, 3715, 3761, and 3781 cm<sup>-1</sup> in the O–H stretching region, and at 1575, 1595, 1610, 1626, 1639, and 1662 cm<sup>-1</sup> in the H–O–H bending region. These multiplets are due to rotating H<sub>2</sub>O in Ar, and are in good agreement with earlier workers. Trace (a) of Figure 4 shows the spectrum of a matrix sample of Ar/H<sub>2</sub>O = 600 over the regions 200–360 and 3560–3800 cm<sup>-1</sup>. Substitution of D<sub>2</sub>O yielded the above bands, weakly, of H<sub>2</sub>O, and bands at 2716 and 3716 cm<sup>-1</sup> for the O–D and O–H stretches of HDO, and bands at 2663, 2746, 2762, 2773, and 2785 cm<sup>-1</sup> for the O–D stretching bands of D<sub>2</sub>O. Bands were also observed in the bending region at 1167, 1177, 1183, 1191, and 1197 cm<sup>-1</sup> for D<sub>2</sub>O, and at 1375, 1388, 1392, 1402, 1418, 1432, and 1442 cm<sup>-1</sup> for HDO. These are all in good agreement with previously reported band positions. When a sample



**Figure 2.** Infrared spectra of the reaction products of CsCl with isotopic water molecules in Ar matrices at 14 K, over the spectral regions 300–500, 2260–2480, and 3180–3240 cm<sup>-1</sup>.

of Ar/H<sub>2</sub><sup>18</sup>O = 600 was studied, bands were observed at 3569, 3699, 3748, and 3766 cm<sup>-1</sup> in the stretching region, and at 1569, 1588, 1603, 1618, 1634, and 1656 cm<sup>-1</sup> in the bending region. While these bands have not been previously reported in Ar matrices, they all show a few wavenumbers shift to lower energy from their <sup>16</sup>O counterparts, and are reasonably assigned to H<sub>2</sub><sup>18</sup>O. It is interesting to note, also, that workers have shown that doping an Ar/H<sub>2</sub>O matrix with another atom or compounds, such as Xe, can partially or entirely eliminate the rotational structure of the H<sub>2</sub>O vibrational bands, presumably by destroying the local structure of the Ar lattice.<sup>21</sup> This effect was observed when NaCl was deposited into these matrices, as well as some of the other salts. In these cases, “nonrotating” H<sub>2</sub>O bands were observed at 3720 and 1595 cm<sup>-1</sup>, in agreement again with earlier workers. Finally, H<sub>2</sub>O has been shown not to rotate in N<sub>2</sub> matrices, and the results here for an N<sub>2</sub>/H<sub>2</sub>O = 600 matrix showed bands at 3554, 3639, 3703, 3720, and 3731 cm<sup>-1</sup> in the O–H stretching region, and at 1600 and 1621 cm<sup>-1</sup> in the H–O–H bending region. These bands are in good agreement with those assigned earlier to the stretching and bending modes of H<sub>2</sub>O and (H<sub>2</sub>O)<sub>2</sub>, with intensity ratios suggesting a predominance of the monomer at these concentrations.

**CsCl + H<sub>2</sub>O.** Two experiments were run in which CsCl was deposited into an Ar matrix without any added H<sub>2</sub>O. However, some residual H<sub>2</sub>O was present, and judging from the band intensities the Ar/H<sub>2</sub>O ratio was about 3000. In these two experiments, with different CsCl levels, weak bands were observed at 462, 697, 3116, and 3204 cm<sup>-1</sup>, with the band at 697 cm<sup>-1</sup> barely perceptible. These bands were somewhat increased in the experiment at higher CsCl level, and appeared to maintain a constant intensity ratio. The two following experiments involved CsCl + Ar/H<sub>2</sub>O, with M/R = 1000 and 600. In both experiments, the four bands listed above grew considerably in intensity, with optical densities of 0.21, 0.06, 0.44, and 0.10, respectively, for the 462, 697, 3116, and 3204 cm<sup>-1</sup> bands, at M/R = 1000. All four of these bands were also quite sharp, as can be seen in traces (a) and (b) of Figure 2. In addition, weak, broad bands were observed at 542, 3175, and 3310 cm<sup>-1</sup>, with OD values less than 0.05. At an M/R of 600, the four bands grew further, and maintained a constant intensity ratio, while the second set of bands at 542, 3175, and 3310 cm<sup>-1</sup> grew more rapidly. When this sample was annealed



**Figure 3.** Infrared spectra of the reaction products of CsBr with isotopic water molecules in Ar matrices at 14 K, over the same spectral region as Figure 2.

to 42 K, the second set of bands grew slightly, while the original four bands decreased a small amount.

Substitution of  $^{18}\text{O}$ -enriched  $\text{H}_2\text{O}$  in one experiment at  $M/R = 600$  led to a shift in each band position, to 460, 695, 3108, and 3194  $\text{cm}^{-1}$ , while the second set of bands (the bands at 542, 3175, 3254, and 3310  $\text{cm}^{-1}$  in the  $^{16}\text{O}$  experiment) was relatively weak and shifted to 541, 3164, 3242, and 3301  $\text{cm}^{-1}$ . The  $^{16}\text{O}$  counterparts were also weakly observed owing to the imperfect enrichment of the  $\text{H}_2^{18}\text{O}$  sample, and impurity  $\text{H}_2\text{O}$  in the system. These bands are displayed in trace (c) of Figure 2.

Deuterium substitution in several different ratios was used in an attempt to clarify the nature of the reaction products. In the first experiment, with an approximate D/H ratio of 6 (taken from the parent band intensities), a distinct counterpart was observed for each of the original four bands listed above, in addition to the parent bands of  $\text{D}_2\text{O}$ , HDO, and  $\text{H}_2\text{O}$ . These new bands were observed at 342, 497, 2318, and 2382  $\text{cm}^{-1}$ . These bands retained, even on deuterium substitution, approximately the same intensity ratios. In addition, a weak band was observed at 2340  $\text{cm}^{-1}$ , and the bands observed in the pure H experiment were observed very weakly from  $\text{H}_2\text{O}$  impurity in the system. An experiment was then run in which the D/H ratio was adjusted to approximately 4. In this experiment, the bands observed in the nearly pure deuterium experiment remained, with similar intensity; the bands due to the pure H species grew slightly; and bands were observed at 2340, 3142, and 401  $\text{cm}^{-1}$ . The band at 2340  $\text{cm}^{-1}$ , which had been much less intense than its neighbors at 2318 and 2382  $\text{cm}^{-1}$  in the experiment with D/H = 6, was now equal in intensity to the 2382- $\text{cm}^{-1}$  band in this D/H = 4 experiment. This experiment is shown in trace (e) of Figure 2.

A final experiment was then conducted in which a D/H ratio of about 1 was used. In this experiment all of the pure D bands were observed, all of the bands observed in the pure H experiment earlier were also observed, and the new bands at 401, 2340, and 3142  $\text{cm}^{-1}$  grew considerably. Three sets of bands then were observed, one of which was observed in the pure  $\text{H}_2\text{O}$  experiments, one of which predominated at very high  $\text{D}_2\text{O}$  levels, and a third set (401, 2340, and 3142  $\text{cm}^{-1}$ ) which was most evident at intermediate D/H levels. These three sets seemed to be internally consistent with respect to intensities over the entire range of experiments.

**RbCl +  $\text{H}_2\text{O}$ .** RbCl was deposited into an argon matrix containing  $\text{H}_2\text{O}$  with  $M/R = 600$  in two different experiments. In addition to the RbCl monomer parent band at 206  $\text{cm}^{-1}$  three new product bands were observed, at 471, 3110, and 3202  $\text{cm}^{-1}$ . In both experiments, the bands were weak but reproducible, and in general agreement with bands observed in the CsCl +  $\text{H}_2\text{O}$  reaction. The overall low yield was probably due to poor oven alignment, rather than overall low reactivity. The effect of oven alignment is similar to that of lowering oven

temperature, in that a lower salt level in the matrix is produced, leading to lower yield of reaction product.

**KCl +  $\text{H}_2\text{O}$ .** KCl was deposited into an Ar matrix in one experiment, with a small amount of impurity  $\text{H}_2\text{O}$  present, and a band at 248  $\text{cm}^{-1}$  was observed which has been assigned previously to Ar matrix-isolated KCl monomer.<sup>22</sup> In addition, weak bands were observed at 475, 3117 and 3201  $\text{cm}^{-1}$ , analogous to the bands in the CsCl/Ar experiment. When an experiment was carried out, reacting KCl and Ar/ $\text{H}_2\text{O} = 600$ , these three bands grew in intensity, and two new weak bands were observed, at 688 and at 242  $\text{cm}^{-1}$ , as a distinct shoulder on the parent KCl monomer. Also, weak bands were observed at 410, 546, 3229, 3288, and 3338  $\text{cm}^{-1}$ . An experiment was also conducted with  $\text{H}_2^{18}\text{O}$ , but the overall yield was low in this experiment. Product bands were observed at 473, 3107, and 3188  $\text{cm}^{-1}$ , but no  $^{18}\text{O}$  counterparts were detected for the 688- and 242- $\text{cm}^{-1}$  bands. No deuterium substitution was attempted with KCl.

**NaCl +  $\text{H}_2\text{O}$ .** Six experiments were conducted in which NaCl was deposited into an Ar matrix without any added  $\text{H}_2\text{O}$ . Some  $\text{H}_2\text{O}$ , nonetheless, was present with the  $M/R$  around 3000. In these experiments, varying the oven temperature for the NaCl evaporation, three major bands were observed, at 469, 3141, and 3251  $\text{cm}^{-1}$ , in addition to parent NaCl and  $(\text{NaCl})_2$  bands at 333, 275, and 226  $\text{cm}^{-1}$ . These bands showed constant relative intensity through the differing experiments, including several experiments in which the matrices were deposited at different cold window temperatures, ranging from 10 to 21 K. This temperature variation appeared to have very little overall effect on product formation. Also, two weak bands were observed at 258 and 290  $\text{cm}^{-1}$ . These have been reported by previous workers,<sup>22</sup> and assigned to aggregate species of NaCl, although such a characterization would be difficult on the basis of the data obtained here. In addition, weak broad bands were detected in the ranges 400–440, 510–520, and 3320–3450  $\text{cm}^{-1}$ . When NaCl was then deposited into matrices of Ar/ $\text{H}_2\text{O} = 600$ , the three major bands grew considerably, and maintained a constant intensity ratio throughout, and the weak broad bands grew as well, but at a different rate than the three major bands. The infrared spectra of all four of the alkali chloride salts with  $\text{H}_2\text{O}$  can be seen in Figure 1. Trace (b) of Figure 4 shows the spectrum of a sample of NaCl + Ar/ $\text{H}_2\text{O}$ , in the NaCl stretching region and in the uncomplexed  $\text{H}_2\text{O}$  region, 3560–3800  $\text{cm}^{-1}$ .

NaCl was also deposited into an  $\text{N}_2$  matrix in one experiment, and bands were observed at 310, 259, and 220  $\text{cm}^{-1}$ , which must be the bands analogous to the three NaCl and  $(\text{NaCl})_2$  parent bands observed in Ar. When NaCl was deposited into a matrix of  $\text{N}_2/\text{H}_2\text{O} = 750$ , three new bands were observed, at 465, 3160, and 3265  $\text{cm}^{-1}$ . These bands were less intense and somewhat broader than the analogous product bands in Ar matrices. When this sample was annealed to 37 K and recooled to 16 K, all three bands grew slightly and in same relative ratios. Since the overall yields in  $\text{N}_2$  were low, no further experiments were conducted in  $\text{N}_2$  matrices.

**CsBr.** Several experiments were carried out in which CsBr was deposited with samples of Ar/ $\text{H}_2\text{O}$  and various isotopic variations. Three major product bands were observed in the reaction of CsBr with a sample of Ar/ $\text{H}_2\text{O} = 600$ , at 435, 3158, and 3229  $\text{cm}^{-1}$ . These bands were all relatively intense and sharp, and resembled closely the product bands in the CsCl +  $\text{H}_2\text{O}$  experiments, with slight shifts in band position. Weak, broad aggregate bands were also observed in the regions 3240–3330 and 390–420  $\text{cm}^{-1}$ . Several deuteration experiments were carried out employing CsBr and samples of Ar/ $\text{D}_2\text{O}$ , with varying degrees of deuteration. In an experiment with D/H = 4, the 435- $\text{cm}^{-1}$  band shifted to 321  $\text{cm}^{-1}$ , and a weaker band appeared at 373  $\text{cm}^{-1}$ , while in the high-frequency region, two new bands appeared at 2338 and 2395

**Table I.** Band Positions ( $\text{cm}^{-1}$ ) of Salt Molecule/ $\text{H}_2\text{O}$  Reaction Products in Argon Matrices

NaCl	258			3141	3251
KCl	242 <sup>c</sup>	475	688	3117	3201
KCl		473		3107	3188
KCN		512		3040	3165
RbCl		471		3110	3202
CsCl		462	697	3116	3204
CsCl <sup>a</sup>		342	497	2318	2382
CsCl <sup>b</sup>		460	695	3108	3194
CsBr		435		3158	3229
CsI		401		3164	3280

<sup>a</sup>  $\text{D}_2\text{O}$ . <sup>b</sup>  $\text{H}_2^{18}\text{O}$ . <sup>c</sup> Possible assignment.

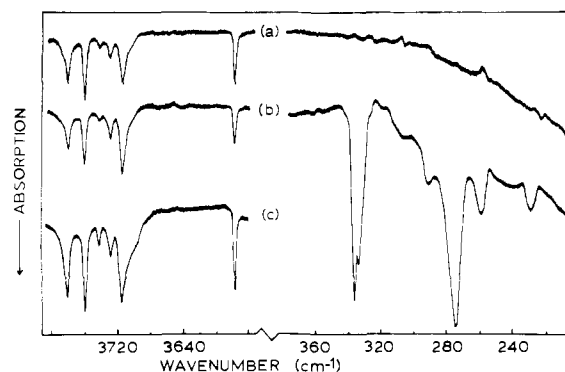
$\text{cm}^{-1}$ , the latter appearing to have a shoulder on the low-energy side. In addition, a weak band was observed near  $3198 \text{ cm}^{-1}$ , in addition to the weak bands at  $3158$  and  $3229 \text{ cm}^{-1}$  due to the pure H species. Lowering the deuterium ratio to  $\text{D}/\text{H} = 1$  caused the three low-frequency bands at  $435$ ,  $373$ , and  $321 \text{ cm}^{-1}$  to appear as a distinct triplet, approximately 1:2:1. In the high-energy region, the bands at  $2338$  and  $2395 \text{ cm}^{-1}$  were weakened, the shoulder at  $2391 \text{ cm}^{-1}$  grew, and resolved into a distinct band, and the weak band at  $3198 \text{ cm}^{-1}$  grew somewhat, while the  $3158$ - and  $3229$ - $\text{cm}^{-1}$  bands grew considerably. These results are all presented in the three traces of Figure 3.

**CsI +  $\text{H}_2\text{O}$ .** CsI was vaporized and deposited into an Ar matrix in one experiment, and into a matrix containing Ar/ $\text{H}_2\text{O} = 600$  in a second experiment. No infrared fundamental of the parent monomeric CsI molecule was expected owing to its low frequency, and this was the case. However, three weak bands were observed in the former experiment, at  $407$ ,  $3164$ , and  $3280 \text{ cm}^{-1}$ , and these bands were again observed in the latter experiment with considerably greater intensity. No deuteration experiments were attempted with CsI.

**KCN +  $\text{H}_2\text{O}$ .** KCN was used in several experiments to determine the role of the halide anion in the complex. KCN has been investigated previously in argon matrices by Margrave and co-workers, and the spectra obtained here for the deposition of KCN into a blank Ar matrix were in good agreement with their results for both monomer and dimer bands.<sup>22</sup> The matrix was a characteristically deep blue color in all experiments employing KCN. When KCN was codeposited with a sample of Ar/ $\text{H}_2\text{O} = 600$ , new bands grew in,  $3040$ ,  $3165$ , and a doublet at  $502$  and  $512 \text{ cm}^{-1}$ , with intensity ratios approximately the same as the analogous bands in the KCl + Ar/ $\text{H}_2\text{O}$  experiments.

## Discussion

The results from the different salt/ $\text{H}_2\text{O}$  experiments can be summarized by observing that strong bands were formed upon reaction of salt molecules with  $\text{H}_2\text{O}$ , and that from the bands obtained two distinct groups may be identified. The first group, typified by the bands at  $462$ ,  $697$ ,  $3116$ , and  $3204 \text{ cm}^{-1}$  in the CsCl +  $\text{H}_2\text{O}$  experiments, appeared even in the most dilute experiments, when water was present only as an impurity, and grew considerably when  $\text{H}_2\text{O}$  was added in subsequent experiments. These four bands also showed the same relative intensities throughout all of the experiments, and the behavior of this group of bands upon dilution indicates that they can be assigned to a 1:1 reaction product of the salt molecule with  $\text{H}_2\text{O}$ . The second group of bands, typified by the bands at  $542$ ,  $3175$ ,  $3254$ , and  $3310 \text{ cm}^{-1}$  in the CsCl +  $\text{H}_2\text{O}$  experiments, appeared only at higher concentrations of the reactants, and particularly at higher concentrations of  $\text{H}_2\text{O}$ . This behavior, coupled with the fact that these bands grew during annealing, suggests that they may be assigned to an aggregate species rather than a well-defined 1:1 reaction



**Figure 4.** Infrared spectra of matrix samples over the spectral ranges 200–360 and  $3560$ – $3800 \text{ cm}^{-1}$ . Trace (a) shows a sample of Ar/ $\text{H}_2\text{O} = 600$ , while trace (b) shows a sample of Ar/ $\text{H}_2\text{O} = 600 + \text{NaCl}$ . Trace (c) depicts a sample of CsBr + Ar/ $\text{H}_2\text{O} = 600$ , over the region  $3560$ – $3800 \text{ cm}^{-1}$ .

product. This assignment is also suggested by the broadness of the infrared absorption bands. This set of bands had a counterpart set at  $541$ ,  $3164$ ,  $3242$ , and  $3301 \text{ cm}^{-1}$  in the CsCl + Ar/ $\text{H}_2^{18}\text{O}$  experiment, and these bands must be assigned to the  $^{18}\text{O}$  analogue of the aggregate species. Not much can be surmised about the nature of the aggregate species, and the following discussion will focus on the three or four bands in each experiment which are associated with the 1:1 reaction product, and whose positions are listed in Table I.

In each experiment, with different alkali halide salts and  $\text{H}_2\text{O}$ , two bands were observed in the region  $3100$ – $3300 \text{ cm}^{-1}$ , while one or two bands were observed between  $400$  and  $700 \text{ cm}^{-1}$  and, in the case of KCl +  $\text{H}_2\text{O}$ , a weak band was observed below  $300 \text{ cm}^{-1}$ . The region above  $3100 \text{ cm}^{-1}$  can reasonably be characterized as the O–H stretching region and, for a 1:1 complex, two such bands are expected, originating from the two O–H stretching modes of the  $\text{H}_2\text{O}$  precursor molecule. In the case of CsCl +  $\text{H}_2\text{O}$  these bands are located at  $3116$  and  $3204 \text{ cm}^{-1}$ , while Table I lists the band positions for the remaining alkali halide/ $\text{H}_2\text{O}$  reaction products. The deuterium results support this assignment—with a distinct deuterium counterpart observed for each band. The  $3116$ - $\text{cm}^{-1}$  band apparently shifts to  $2318 \text{ cm}^{-1}$ , and the  $3204$ - $\text{cm}^{-1}$  band shifts to  $2382 \text{ cm}^{-1}$ . These shift ratios, 1.34 and 1.34, respectively, are of a magnitude expected for an O–H stretching vibration, and are very close to the shift ratios for  $\nu_1$  and  $\nu_3$  of  $\text{H}_2\text{O}$ . Also, the  $2382$ - $\text{cm}^{-1}$  band has the same intensity relative to the  $2318$ - $\text{cm}^{-1}$  band that the  $3204$ - $\text{cm}^{-1}$  band has to the  $3116$ - $\text{cm}^{-1}$  band, supporting this mapping as well. Equally important, as the D/H ratio was reduced, and as more hydrogen was introduced into the system, two new bands grew in, one between the two deuterium counterparts at  $2345 \text{ cm}^{-1}$ , and the other between the two hydrogen counterparts at  $3142 \text{ cm}^{-1}$ . These bands have the right position and intensities to be assigned to the two stretching modes of CsCl/ $\text{HDO}$  complex. In such a complex one would expect one vibration of nearly pure O–H character and one of nearly O–D character. This is exactly the behavior observed here and is precisely the behavior of isolated HDO, where one stretching mode is near that of  $\text{D}_2\text{O}$  and the other is near  $\text{H}_2\text{O}$ . The above results suggest strongly that the reaction complex contains two equivalent hydrogen atoms and, if this were not the case, then a considerably different spectrum would have been obtained.

It is apparent from the spectra that there is an intensity reversal of  $\nu_1$  and  $\nu_3$  from the spectra of the free  $\text{H}_2\text{O}$  molecule.  $\nu_3$  is the more intense band for  $\text{H}_2\text{O}$ , yet the band observed here for the complex which correlates with  $\nu_1$  is considerably more intense. This effect has been observed previously and discussed

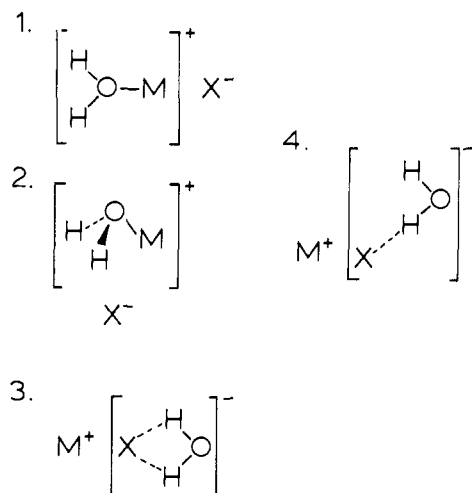


Figure 5. Four possible structures for the 1:1 complex of alkali halide salt molecules with H<sub>2</sub>O isolated in argon matrices.

in terms of the Ferguson–Matson–Friedrich–Person model,<sup>23</sup> which demonstrates that an intensity enhancement is expected for totally symmetric vibrational modes of charge transfer complexes. As a consequence, this result is not unexpected here, and points toward a charge transfer or ion transfer complex.

The results employing <sup>18</sup>O-enriched H<sub>2</sub>O suggest also that the reaction occurring is forming a 1:1 complex. The shift in the band positions with H<sub>2</sub><sup>18</sup>O is almost the exact same shift as observed for free H<sub>2</sub><sup>18</sup>O relative to H<sub>2</sub><sup>16</sup>O, again suggesting an O–H stretching mode. More importantly, a small amount of residual H<sub>2</sub><sup>16</sup>O was present in these experiments and, in the case of the 3204-cm<sup>-1</sup> band, a distinct doublet was observed with no intermediate bands suggesting a species with only a single water molecule. It is, of course, possible that the complex contains two water molecules, whose vibrations are nearly completely uncoupled, but the concentration studies, along with the <sup>18</sup>O data, tend to refute this possibility.

One must also consider the possibility that the observed complex is between the salt dimer, (MX)<sub>2</sub>, and a water molecule, since the salt vapor over the solid at this temperature does contain a considerable fraction of the dimer. This is not likely, however, since the dimer is very strongly bound, and the strength of interaction with H<sub>2</sub>O is not great enough to disrupt the dimer structure. Also, if the salt dimer/H<sub>2</sub>O complex accounted for the observed product species, it would imply that a complex is not formed between the salt monomer and H<sub>2</sub>O, which is not a likely circumstance.

In experiments with alkali halide salt molecules and H<sub>2</sub>O, one or two bands were also observed in the region 400–700 cm<sup>-1</sup>. Specifically, a band was observed between 400 and 480 cm<sup>-1</sup> in each case, and in several experiments a second band was observed near 700 cm<sup>-1</sup>. The 1:1 reaction complex, almost independent of geometry (which will be discussed in a later section of the paper), will be expected to have two deformation modes which, owing to the lightness of the hydrogen atoms, should be essentially hydrogen vibrations. The deuterium shifts in the CsCl experiments suggest that this is the case, with a strong deuterium shift observed for both the 462- and 697-cm<sup>-1</sup> bands, to 342 and 497 cm<sup>-1</sup>. The shifts here are 1.35 and 1.40, respectively. Again, the mixed D/H experiments are very informative, in that a distinct triplet is observed for the 462-cm<sup>-1</sup> band. The pure deuterium counterpart was observed at 342 cm<sup>-1</sup> and an intermediate band grew in with decreasing D/H ratio, at 401 cm<sup>-1</sup>. This distinct triplet lends compelling support for the conclusion that the 1:1 complex contains two equivalent hydrogen atoms. This should be the case as well for the 697-cm<sup>-1</sup> band and its deuterium counterparts, but this

Table II. Gas-Phase Energetics of Alkali Metal Cation and Halide Anion Hydration<sup>a</sup>

M <sup>+</sup>	M <sup>+</sup> + H <sub>2</sub> O → (H <sub>2</sub> OM) <sup>+</sup> -ΔH, kcal/mol
Li <sup>+</sup>	34.0
Na <sup>+</sup>	24.0
K <sup>+</sup>	17.9
Rb <sup>+</sup>	15.9
Cs <sup>+</sup>	13.7
X <sup>-</sup>	X <sup>-</sup> + H <sub>2</sub> O → (XH <sub>2</sub> O) <sup>-</sup> -ΔH, kcal/mol
F <sup>-</sup>	23.3
Cl <sup>-</sup>	13.1
Br <sup>-</sup>	12.6
I <sup>-</sup>	10.2

<sup>a</sup> I. Dzidic and P. Kebarle, *J. Phys. Chem.*, **74**, 1466 (1970); M. Arshadi, R. Yamdagni, and P. Kebarle, *ibid.*, **74**, 1475 (1970).

was the weakest band system detected and no intermediate band was detected, presumably owing to low intensities.

The final band observed in this sequence of experiments was a weak band appearing as a shoulder in the low-energy side of the 248-cm<sup>-1</sup> KCl parent band on the KCl + H<sub>2</sub>O experiment in Ar. This band must be associated with a product species as well, as it is not detected in the KCl + Ar experiments, but is quite clear in the KCl + Ar/H<sub>2</sub>O experiments. Depending on the nature of the complex, this band may either be interpreted as a perturbed KCl vibration in the complex or as, perhaps, a K–O stretching vibration. Consideration of the structure of the complex, in the next portion of the paper, may aid in the assignment of this band.

Regardless of this assignment, the bands associated with the 1:1 salt/H<sub>2</sub>O complex can be assigned to two O–H stretching vibrations, a hydrogen deformation vibration (or two in the case of KCl and CsCl + H<sub>2</sub>O), and possibly a metal–oxygen stretching band. The evidence from all of these band assignments also clearly supports a complex in which the two hydrogen atoms are equivalent.

Determination of the structure or geometry of the complex is of considerable interest as well. The gas-phase heats of reaction from Kebarle's work are tabulated in Table II, and these values suggest that the binding of an alkali metal cation to the lone pairs on H<sub>2</sub>O is generally stronger than the hydrogen bonding of the halide anion to the hydrogens on the water molecule, with the exception of the fluoride anion, which has not been considered here. The use of ion cyclotron resonance (ICR) has allowed for further determination of the strengths of binding of alkali metal cations to a large number of bases,<sup>24</sup> suggesting that binding energies up to 50 kcal/mol can occur for Li<sup>+</sup>. Theoretical calculations also tend to support the binding of a cation preferentially over the hydrogen bonding of the anion.

Four possible structures can be envisioned for such a complex, and are depicted in Figure 5. These are undoubtedly not all of the possibilities but are the major ones. Structure 4, which employs an unsymmetrical hydrogen bond, can be ruled out quickly on the basis of equivalence of the hydrogen atoms, which has been demonstrated above. If this were, in fact, the geometry, one would expect to see a single hydrogen stretching mode of the hydrogen-bonded hydrogen shifted well down from H<sub>2</sub>O and another hydrogen stretching frequency nearly equal to that of free H<sub>2</sub>O. A careful search for such a band was made, and no such band was observed. Figure 4 shows this search for the NaCl + Ar/H<sub>2</sub>O and CsBr + Ar/H<sub>2</sub>O experiments by comparison to trace (a), Ar/H<sub>2</sub>O with no added salt. This is in agreement with the fact that two bands were observed considerably shifted from free H<sub>2</sub>O.

Structure **3**, involving a symmetrically hydrogen-bonded species, fulfills the requirement of two equivalent hydrogen atoms. The vibrational modes of this complex should show virtually no dependence on the nature of the metal cation, as the cation simply serves as a counterion for stability. However, a dependence was observed, although relatively small, as shown in Table I. Secondly, the O–H stretching modes should show a strong dependence on the halide anion used in the complex, since the hydrogen bonding capabilities of the halide anions vary considerably from  $\text{Cl}^-$  to  $\text{I}^-$ , and thus the band positions should shift accordingly. According to the relation proposed by Pimentel and co-workers,<sup>25</sup> this band position should depend directly on the proton affinity of the base or anion, and these are known to range from 333 kcal/mol for  $\text{Cl}^-$  to 313  $\text{cm}^{-1}$  for  $\text{I}^-$ .<sup>26</sup> The results with KCN show this as well, since  $\text{CN}^-$  should have considerably different hydrogen bonding characteristics, yet  $\text{KCN}\cdot\text{H}_2\text{O}$  showed a similar spectrum to  $\text{KCl} + \text{H}_2\text{O}$ . These band positions are also listed in Table I.

One can make an estimate of the O–H stretching frequencies in a purely hydrogen-bonded complex such as structure **3** by comparison of the hydrogen stretching frequencies of a  $\text{Cl}^-$  anion hydrogen bonded to  $\text{NH}_3$  (a weaker acid) and to  $\text{HCl}$ , a stronger acid, since the shift in the hydrogen bond vibrational frequency of a series of acids with a single Lewis base has been shown to depend monotonically on the acid strength of the hydrogen donor.<sup>25</sup> In the former case, the N–H– $\text{Cl}^-$  stretching band<sup>27,28</sup> fell between 1900 and 2600  $\text{cm}^{-1}$ , while in the latter case,<sup>16</sup> the Cl–H– $\text{Cl}^-$  band fell near 700  $\text{cm}^{-1}$ .  $\text{H}_2\text{O}$ , with intermediate acidity and hydrogen bonding character, should yield a band between these two extremes, if structure **3** is the correct geometry. This is not observed, as the bands were detected in the 3100- $\text{cm}^{-1}$  region suggesting that a purely hydrogen-bonded species is not formed. One theoretical calculation has been performed on the  $\text{Cl}^- \cdot \text{H}_2\text{O}$  system, and indicated that the bonding was largely electrostatic, with little charge migration.<sup>29</sup> However, this work did not predict frequency shifts for the hydrogen stretching frequencies, and cannot be used for direct comparison here.

Generally, the band shapes of hydrogen-bonded stretching vibrational bands are quite broad,<sup>30</sup> for both solution phase hydrogen-bonded species and matrix-isolated hydrogen-bonded acid/base pairs.<sup>16,31,32,33</sup> This is not the case here, suggesting again that the interaction is not purely a hydrogen bonding interaction. Gas-phase energetics argue against structure **3** since the interaction of an isolated metal cation with  $\text{H}_2\text{O}$  has been shown to be stronger than an isolated halide anion with  $\text{H}_2\text{O}$ . All of these points together serve to rule against the symmetrically hydrogen-bonded complex.

The first complex, **1**, in which a planar cationic species is formed through the interaction of the metal cation with the two lone pairs of the oxygen, satisfied the requirement of two equivalent hydrogens as well. However, the position of the O–H stretching bands, near 3100–3200  $\text{cm}^{-1}$ , rules against this structure. It would be hard to envision a complex in which the alkali metal cation withdraws sufficient electron density from the O–H bonds to lower the vibrational frequency about 600  $\text{cm}^{-1}$ . Recent studies have been directed at determining the effect of an isolated cation on the vibrations of the water molecule, and the best estimates available now suggest that the O–H stretching frequencies will shift a few wavenumbers at most.<sup>34</sup> The magnitude of these shifts are more indicative of some hydrogen-bonding interaction, where very large shifts are common. Moreover, the band positions do show a slight halide anion shift, which would not be expected for a planar cationic species where the halide anion is serving strictly as a counterion. This planar structure then is not probable either.

The final structure depicted here, **2**, satisfies all of the points mentioned above. In this complex, the alkali metal cation binds

to the oxygen of the water molecule, as suggested by gas-phase energetics. However, the cation formed is pyramidal rather than planar, brought about by the interaction with a single lone pair on the oxygen, rather than by equal interaction with both lone pairs. The addition of an  $\text{H}^+$  to  $\text{H}_2\text{O}$  to form  $\text{H}_3\text{O}^+$  yields a pyramidal species, so it is not surprising that the addition of a metal cation  $\text{M}^+$  to  $\text{H}_2\text{O}$  should lead to a pyramidal species. In this pyramidal configuration the halide anion serves as a counterion, but in doing so can interact with all of the centers of positive charge in the complex, including the hydrogens as well as the alkali metal. This would lead to a partial (nonplanar) hydrogen-bonding interaction, and shifts of the O–H stretching frequency comparable to those observed. This structure should also lead to both a dependence on the cation and on the anion for all of the vibrational modes, as was the case. The gas-phase energetics also would support this particular structure, and the observation of a metal–oxygen stretching frequency could be accounted for as well. This geometry does not require the anion to sit symmetrically at the base of the pyramidal structure, but rather it should favor the center of largest positive charge, which will undoubtedly still be the metal atom. The geometry will be  $C_s$  in this complex, and this particular structure fits all of the available data.

It is also worth noting that in the gas-phase water dimer,  $(\text{H}_2\text{O})_2$ , the structure is open, and the oxygen atom involved in the hydrogen bond is bonded in a pyramidal arrangement, not in a planar configuration.<sup>35</sup> This, too, supports the structure proposed here.

One other possible structure is a planar structure in which the metal cation binds to the oxygen, while the halide anion symmetrically hydrogen bonds to the two hydrogens of the water molecule, a composite of structures **1** and **3**. However, this structure can be ruled out by observing that it is very unlikely that the major centers of positive and negative charge would be so completely separated, when the pyramidal geometry would allow for considerably greater attractions. Moreover, it is hard to envision how such a complex could be formed, for it would require the complete rupture of the M–Cl bond during complex formation.

The pyramidal  $C_s$  structure for the complex should have, as noted earlier, two hydrogen stretching modes, which are observed. The complex should also have two hydrogen deformation modes, originating with the  $A_1$  mode of the pyramidal  $C_{3v}$  molecule, and one of the components of the doubly degenerate E mode of the  $C_{3v}$  molecule, since the degeneracy is broken upon reduction of the symmetry to  $C_s$ .<sup>36</sup> This accounts for the two deformation modes observed for a number of the complexes. For many of the complexes only one deformation mode was observed, while the second was probably not observed for lack of intensity. When this second band was observed, as in the  $\text{CsCl} + \text{H}_2\text{O}$  experiment, it was quite weak. In addition, this pyramidal species should show a metal–oxygen stretching mode, but this would likely lie below 200  $\text{cm}^{-1}$ , the instrumental cutoff, except possibly for the  $\text{Na}^+$  and  $\text{K}^+$  complexes. Such a band may have been observed in the  $\text{KCl}$  experiment at 242  $\text{cm}^{-1}$ , while in the  $\text{NaCl}$  experiment, the only candidate is the band at 258  $\text{cm}^{-1}$ . This has been assigned by previous workers to an aggregate species of  $\text{NaCl}$ .<sup>22</sup> However, if these workers also had  $\text{H}_2\text{O}$  present as an impurity, then the band may have been misassigned. Insufficient evidence is available to make a definitive assignment of this band, either to an aggregate species or to the Na–O stretch of the  $\text{NaCl}\cdot\text{H}_2\text{O}$  complex. The infrared spectrum of crystalline  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$  has been investigated, and the complex is shown to be bound through  $\text{Li}^+$  cation to the water molecule.<sup>37</sup> In the spectrum, two librational modes of the water molecule were observed between 400 and 600  $\text{cm}^{-1}$ , analogous to the two deformation modes observed here. These workers also observed the Li–O stretching band near 400  $\text{cm}^{-1}$ , which leads to a

prediction, on the basis of mass and force constants, of frequencies below  $200\text{ cm}^{-1}$  for the metal-oxygen stretching frequency in most of the complexes studied here. Finally, one would expect a hydrogen bending mode analogous to the  $1600\text{-cm}^{-1}$  bending mode of free  $\text{H}_2\text{O}$ , perhaps in the region near  $1600\text{ cm}^{-1}$ . Such a band was not observed, although a careful search was made. The lack of observation could be due either to lack of intensity or lack of a shift from free  $\text{H}_2\text{O}$ , which contributed a number of bands in the  $1600\text{-cm}^{-1}$  region. Regardless, lack of observation of such a band cannot detract significantly from the overall assignments made here.

One cannot overlook the possibility that more than one complex is formed, but owing to band shifts and/or absorption coefficients, only one form is detected. This seems unlikely, however, since even a  $2\text{-}4\text{-cm}^{-1}$  shift would have been observed, since all bandwidths were quite sharp. A careful search was carried out in the region of uncomplexed water particularly, as evidenced in Figure 4, and no new bands were observed, even with very small shifts from  $\text{H}_2\text{O}$ . The possibility of a complex with very low absorption coefficients remains, but in view of the ionic nature of the complex, lack of observation of a major product species for this reason is not likely.

Transition metal aquo complexes, of the form  $\text{M}(\text{H}_2\text{O})_n^{m+}$ , can serve as a model for predicting vibrational frequencies in alkali metal/ $\text{H}_2\text{O}$  complexes. In the transition metal complexes, two hydrogen deformation modes have been observed,<sup>38-40</sup> one between  $450$  and  $650\text{ cm}^{-1}$  and the other between  $650$  and  $850\text{ cm}^{-1}$ . Since the interaction between an alkali metal cation and  $\text{H}_2\text{O}$  is presumably slightly weaker than the interaction between a transition metal cation and  $\text{H}_2\text{O}$ , one might predict slightly lower frequencies for the  $\text{M}^+\text{H}_2\text{O}$  complexes postulated here, and this fits well with the one or two low-frequency bands observed in this work. Also, the metal-oxygen stretching mode has been observed for the transition metal complexes, and the band falls between  $300$  and  $500\text{ cm}^{-1}$  in each case. With the slightly weaker interaction, and subsequently lower force constant, values below  $300\text{ cm}^{-1}$  are not unexpected for  $\text{Na}^+$  and  $\text{K}^+$ , and below  $200\text{ cm}^{-1}$  for the remaining alkali metal cations. The model of the transition metal aquo complexes, which are known to be bound through the oxygen lone pairs to the transition metal, fits the observed spectra reasonably well, and supports assignment to a complex which does involve metal cation- $\text{H}_2\text{O}$  interactions, such as structure 2.

The results of Devlin and co-workers should be considered at this point. In three separate studies they have investigated the infrared spectrum of salt-water complexes. In the first study,<sup>7</sup>  $\text{H}_2\text{O}$  was deposited into glasses formed by the evaporation and condensation of alkali perchlorate salts. These mixtures, at low temperatures, yielded two band systems in the O-H stretching region. One set was relatively sensitive to the nature of the alkali metal cation, while the other was not. This was interpreted to indicate that two types of interactions were occurring—an inner sphere coordination of the metal cation to the water and an outer sphere hydrogen bonding interaction of the  $\text{H}_2\text{O}$  to the anion. This supports the observation here that both types of interactions can occur, and that the metal-base interaction is quite strong. It must be noted, however, that this set of experiments by Devlin and co-workers is quite different in nature from those conducted here.

In the second study,<sup>8</sup> Devlin and co-workers deposited alkali metal nitrates and chlorates into glassy  $\text{H}_2\text{O}$  at  $12\text{ K}$ , and measured the strength of the interaction through the splitting of the  $\nu_3$  band of  $\text{NO}_3^-$  and the decreasing frequency of  $\nu_1$  of  $\text{ClO}_3^-$ . They conclude that the polarizing power of the cation is sharply reduced via interaction with the  $\text{H}_2\text{O}$  molecules, and that the interaction is one in which the cation directly interacts with the lone electron pairs on the water molecule, as is postulated for structure 2.

The third study was done by co-condensing alkali nitrate salts in argon matrices doped with  $\text{H}_2\text{O}$ , in some respects similar to the studies here.<sup>9</sup> They concluded that the cation bound to the  $\text{H}_2\text{O}$  in all cases, and that the salt  $\text{M}^+\text{NO}_3^-$  remained a contact ion pair, in qualitative agreement with the results here. It should be noted, though, that these studies were carried out at much higher  $\text{H}_2\text{O}$  levels, 6 to 100%  $\text{H}_2\text{O}$ , while the work here, aimed at the 1:1 complex, was carried out at 0.10-0.02%  $\text{H}_2\text{O}$  in Ar. Also, Devlin and co-workers deposited for much shorter times, and monitored the very intense  $\text{NO}_3^-$  bands as a measure of the interaction. Consequently, they did not observe bands in the  $3100\text{-cm}^{-1}$  region analogous to those observed in this work. It may be presumed, though, that under similar conditions of deposition, concentration, and length, similar bands would have been observed.

A comparison to the numerous theoretical efforts concerning this interaction should be made as well.<sup>11-14</sup> These calculations were generally made for  $\text{Li}^+$  (although  $\text{Na}^+$  and  $\text{K}^+$  were considered in one case),<sup>12</sup> and the geometry of lowest total energy was found to be planar. However, this does not take into account the presence of a halide anion as a counterion, so that the comparison in geometry is not entirely valid. Clementi<sup>12</sup> also predicts vibrational frequencies for the metal-oxygen stretching vibration, and the two deformation modes. He predicts the two deformation frequencies in the  $300\text{-}400\text{-cm}^{-1}$  range, with slight dependence on the metal cation, which is in reasonable agreement with the observed frequencies,  $462$  and  $697\text{ cm}^{-1}$  for the  $\text{CsCl}/\text{H}_2\text{O}$  complex. He also predicts that the metal-oxygen stretching frequencies will lie quite low, below  $250\text{ cm}^{-1}$ , except for  $\text{Li}^+$ , which was not studied here. Clementi's Mulliken population analysis suggests that very little electron density is transferred to the metal cation (about  $0.01\text{ e}^-$ ), and some electron density is transferred to the oxygen from the hydrogen atoms ( $0.1\text{-}0.2\text{ e}^-$ ), leaving the metal cation still the largest center of positive charge.<sup>12</sup> Also, this predicts withdrawal of electron density from the hydrogen atoms from which one may infer a weakening of the O-H bonds and a subsequent lowering of the vibrational frequencies as observed, although the major portion of the lowering of the O-H stretching frequency must come through hydrogen bonding.

## Conclusions

In each of the reactions of salt molecules with  $\text{H}_2\text{O}$  in Ar matrices, three or four major bands were observed which could be assigned to 1:1 complex, while additional bands were observed at higher concentrations of reactants, and have been assigned to aggregate species. The observed bands of the 1:1 complex were assigned to the two O-H stretching modes of the complex, and the one or two low-frequency bands to the hydrogen deformation modes in the complex. The favored geometry of the complex on the basis of all of the evidence available is a pyramidal geometry in which the metal cation is bonded to the oxygen atom of the water molecule and the halide anion sits as a counterion below the base of the pyramid, interacting with the metal cation and the hydrogens of the water molecule. This geometry predicts all of the observed features of the infrared spectrum of these complexes, and is in qualitative agreement with the theoretical calculations on alkali metal cation- $\text{H}_2\text{O}$  complexes.

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## References and Notes

- (1) C. U. Smith, "The Brain, Towards an Understanding", Putnam, New York, N.Y., 1970.
- (2) "Alkali Metal Complexes", *Struct. Bonding (Berlin)*, **16** (1973).

- (3) K. Balasubrahmanyam and G. J. Janz, *J. Solution Chem.*, **1**, 445 (1972).  
 (4) D. E. Irish, *Ionic Interact.*, **2**, 187 (1971).  
 (5) I. Dzidic and P. Kebarle, *J. Phys. Chem.*, **74**, 1466 (1970).  
 (6) M. Arshadi, R. Yamdagni, and P. Kebarle, *J. Phys. Chem.*, **74**, 1475 (1970).  
 (7) G. Ritzhaupt and J. P. Devlin, *Inorg. Chem.*, **16**, 486 (1977).  
 (8) (a) N. Smyrl and J. P. Devlin, *J. Phys. Chem.*, **77**, 3067 (1973); (b) *J. Chem. Phys.*, **61**, 1596 (1974).  
 (9) G. Ritzhaupt and J. P. Devlin, *J. Phys. Chem.*, **79**, 2265 (1975).  
 (10) See, for example, D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968); J. Braunstein, *J. Phys. Chem.*, **71**, 3402 (1967).  
 (11) E. Clementi and H. Popkie, *J. Chem. Phys.*, **57**, 1077 (1972).  
 (12) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **58**, 1689 (1973).  
 (13) K. G. Spears and S. H. Kim, *J. Phys. Chem.*, **80**, 673 (1976).  
 (14) K. G. Spears, *J. Phys. Chem.*, **81**, 186 (1977).  
 (15) B. S. Ault and L. Andrews, *J. Am. Chem. Soc.*, **97**, 3824 (1975).  
 (16) B. S. Ault and L. Andrews, *J. Chem. Phys.*, **63**, 2466 (1975).  
 (17) B. S. Ault and L. Andrews, *J. Am. Chem. Soc.*, **98**, 1591 (1976).  
 (18) E. Catalano and D. E. Milligan, *J. Chem. Phys.*, **30**, 45 (1959).  
 (19) J. A. Glaser, *J. Chem. Phys.*, **33**, 252 (1960).  
 (20) R. L. Reddington and D. E. Milligan, *J. Chem. Phys.*, **37**, 2162 (1962).  
 (21) G. P. Ayers and A. D. E. Pullin, *Spectrochim. Acta, Part A*, **32**, 1629, 1641 (1976).  
 (22) Z. K. Ismail, R. H. Hauge, and J. L. Margrave, *J. Mol. Spectrosc.*, **54**, 402 (1975).  
 (23) H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).  
 (24) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 5920 (1975).  
 (25) B. S. Ault, E. A. Steinback, and C. C. Pimentel, *J. Phys. Chem.*, **79**, 615 (1975).  
 (26) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 257 (1971).  
 (27) M. P. Marzocchi, C. W. Fryer, and M. Bambagiotti, *Spectrochim. Acta*, **21**, 155 (1964).  
 (28) J. A. Frietag, M.S. Thesis, University of Cincinnati, 1966.  
 (29) H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, **58**, 5627 (1973).  
 (30) G. C. Pimentel and A. L. McClellan "The Hydrogen Bond", W. H. Freeman, San Francisco, Calif., 1960.  
 (31) B. S. Ault and G. C. Pimentel, *J. Phys. Chem.*, **77**, 57 (1973).  
 (32) B. S. Ault and G. C. Pimentel, *J. Phys. Chem.*, **77**, 1649 (1973).  
 (33) P. T. T. Wong and E. Whalley, *J. Chem. Phys.*, **62**, 2418 (1975).  
 (34) H. P. Hayward, private communication.  
 (35) J. A. Odutola and T. R. Dyke, 32nd Symposium on Molecular Spectroscopy, Columbus, Ohio, 1977, Paper RC6.  
 (36) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970, p 95.  
 (37) S. Meshitsuke, H. Takahashi, and K. Higasi, *Bull. Chem. Soc. Jpn.*, **44**, 3255 (1971).  
 (38) I. Gamo, *Bull. Chem. Soc., Jpn.*, **34**, 760, 765, 1430, 1433 (1961).  
 (39) G. Sartori, C. Furlani, and A. Damiani, *J. Inorg. Nucl. Chem.*, **8**, 119 (1958).  
 (40) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

## Reaction of Uranocenes with Nitro Compounds<sup>1</sup>

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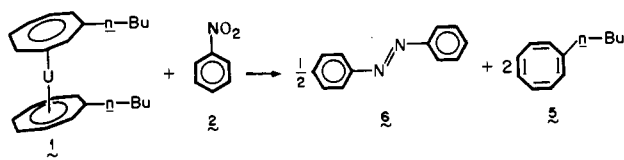
**Abstract:** Uranocenes (di- $\eta^8$ -cyclooctatetraeneuranium) are relatively stable to many neutral oxygen-containing organic compounds but react rapidly with aromatic and aliphatic nitro compounds to liberate the cyclooctatetraene ligand in quantitative yield and form azo compounds, often in good yield but in some cases with formation also of the corresponding amines. *p*-Nitrotoluene reacts more slowly than nitrobenzene. Additional studies of reaction mechanism show that free nitro radical anions or nitrenes do not appear to be involved, but free nitroso compounds are probable intermediates. Azoxy compounds react more slowly with uraniumocenes and cannot be intermediates in the reactions of nitro compounds. The reaction has few analogies.

### Introduction

Since the discovery of uraniumocene in 1968,<sup>2</sup> we and others have investigated the generality of the synthesis as well as the physical and chemical properties of the parent compound and its derivatives.<sup>3-6</sup> Studies have been made of hydrolytic reactions of uraniumocenes,<sup>4a,7</sup> and some studies of alkyl lithium substitution on the carbon ring of appropriately substituted uraniumocenes have been reported.<sup>4c,8</sup> This paper extends uraniumocene chemistry into synthetic organic chemistry, focusing on its properties as a reagent for the reduction of nitro compounds and related derivatives. In addition to synthetic potential we have also studied corresponding reaction mechanisms because organoactinide chemistry is a relatively new field and few such studies are presently available.

### Results

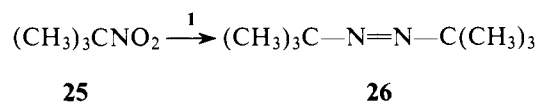
In screening tests, acetone, dimethyl sulfoxide, phenyl isocyanate, iodobenzene, styrene oxide, hexamethylphosphoric triamide, ethylene carbonate, and trimethyl phosphate were treated with 1,1'-di-*n*-butyluranocene (**1**) in THF or toluene,



and were found not to decolorize the green solutions within 1 h. However, nitrobenzene (**2**), 2-methoxynitrobenzene (**3**), and 1,2-dinitrobenzene (**4**), even when specially purified, instantly decomposed uraniumocene solutions and gave brown precipitates. In such experiments the use of substituted uraniumocenes is more convenient than uraniumocene itself because of the low solubility of the parent compound.

These preliminary studies led to larger scale experiments with nitro compounds. Treatment of **1** with 1 equiv of **2** resulted in the recovery of 85% of the *n*-butylcyclooctatetraene (**5**) originally present in the uraniumocene, and gave a 61% yield of azobenzene (**6**). A series of substituted nitroarenes was studied, and the results are summarized in Tables I and II. These yields are probably low owing to handling losses on the small scale used (often less than 100 mg of nitro compound). The recovery of **5** was 85–100% in most of these reactions.

Three aliphatic nitro compounds were studied. 2-Methyl-2-nitropropane (**25**) reacts rapidly with **1** to give a mixture of **5** and 1,1,1',1'-tetramethylazoethane (**26**). Further purification was difficult, since the azo compound is rather volatile.



1-Nitro-1-phenylpropane (**27**) gave small amounts of impure azo compound **28** and propiophenone (**29**). 2-Nitro-2-