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A Theoretical Investigation of the Geometries, Vibrational Frequencies, and Binding Energies of Several Mixed Alkali Halide Dimers

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A theoretical investigation of the geometries, vibrational frequencies, and binding energies of several mixed alkali halide dimers

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Results are presented from *ab initio* calculations on several mixed alkali halide dimers made up of Li, Na, F, and Cl. All of the dimers are investigated at the restricted Hartree–Fock level to provide *ab initio* estimates of geometries, vibrational frequencies, and binding energies. The dimer $LiNaF_2$ is then treated using a variety of basis sets at the Hartree–Fock level, as well as at correlated levels (second-order Møller–Plesset and coupled-cluster singles and doubles) to examine the sensitivity of the calculations to use of higher levels of theory. The results are then compared to the experimental data available for the $LiNaF_2$ molecule, previous theoretical results for the monomers, and recent semiempirical calculations on the mixed dimers.

I. INTRODUCTION

The study of alkali halide clusters has been a fertile ground for the interplay between experiment and theory for over 30 years.[1–26] This is in part due to the idea that the largely Coulombic nature of these compounds should allow one to understand clusters and solids based on a simple combination of ionic attractions and Pauli repulsive interactions, perhaps augmented with terms related to ion polarizability in the cluster. The vapors of alkali halides have long been known to contain small clusters. In most cases the dimer predominates, but in the lighter species one also finds trimers.[19] A variety of early experimental studies attempted to characterize the symmetrical dimers by depositing them in rare-gas matrices and then performing infrared (IR)-spectroscopy on the three allowed vibrational modes of the D_{2h} ground state conformer of the dimers.[17,19–21] Klemperer and Norris[18] studied lithium halide dimers directly in the gas phase. In all of the above experiments the only structural information obtained was inferred by comparison with theoretical models used to assign the vibrational frequencies. More recently work has appeared using electron diffraction techniques to examine the geometries of symmetrical dimers in the gas phase.[9–13] This work has been compared with *ab initio* results for the lighter alkali and halide species, and generally good agreement has been obtained.[23]

The bulk of the theoretical work on the dimers was based on simple models of the ions and their interactions.[1–8,14–16,22] These models have the advantages of computational and conceptual simplicity and are semiquantitative in structure predictions when compared with the recent electron-diffraction data. Models of this type have also been used to study large alkali halide clusters.[14–16] *Ab initio* methods have also been applied to the study of small to moderate-sized clusters.[23–26] However, it appears that no *ab initio* results have been presented for the mixed dimers.

The mixed dimers have been the subject of much less experimental work. In a study of $LiNaF_2$ Cyvin *et al.*[21] attempted to assign vibrational frequencies. They used a simple model to estimate vibrational frequencies for the mixed dimer and then associated close lines in the IR with some of these transitions. A later Fourier transform infrared (FTIR) study by Ramondo *et al.*[22] attempted to sort out transitions due to the mixed and symmetrical dimers in rare gas matrices and used a polarizable ion model to guide assignments. The two studies are in significant disagreement over the peak assignments. More recently theoretical results[22(b)] based on the model used to interpret the Ramondo *et al.* experiments have been presented which treat geometries and binding energies of many mixed dimers.

Given the relative success of our previous results[23] in comparison with the electron diffraction data on the symmetrical dimers, it was felt useful to address some of the mixed dimers using similar techniques. The present article treats several mixed dimers and has two main purposes. First, results are presented for geometries, vibrational frequencies, and binding energies for four mixed dimers containing Li, Na, F, and Cl, all at the restricted Hartree–Fock (RHF) level in a basis set comparable to that used for the symmetrical dimers.[23] $LiNaF_2$ is then used as a model system to explore the sensitivity of the results to basis set expansion at the uncorrelated level, as well as to the inclusion of correlation at the second-order Møller–Plesset (MP2), coupled cluster singles and doubles (CCSD) and CCSD(T) (CCSD with noniterative inclusion of connected triple excitations[27]) levels of theory. The $LiNaF_2$ calculations can then be used as a tentative guide for estimated correlation and basis set effects on the RHF results for the remaining dimers.

The article is organized as follows. In Sec. II the computational methods and basis sets are presented. In Sec. III our results are presented, and in Sec. IV the principal findings are discussed and compared with previous theoretical and experimental results.

II. THEORETICAL METHODS

A variety of program suites were used in the present study. Some of the RHF and MP2 calculations were performed using GAMESS.[28] The MP2 and CCSD vibrational

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frequency calculations and some geometry optimizations were performed using G92.[29] We estimate that the precision of these geometries is ± 0.0005 Å. All other geometries are expected to be precise to ± 0.0002 Å. Most monomer and dimer CCSD calculations, and many of the RHF optimizations, especially those in the largest basis sets were done using PSI.[30]

Several different basis sets were used in the present study, many of which contain extended sets of polarization functions. Rather than encumbering the text with complex notations, they will be denoted based on the *sp* set from which the final basis set is built, and then numbered sequentially according to increasing augmentation. Thus the 6-31G(1) is the first 6-31G basis described below, whereas 6-311G(3) is the third 6-311G-based function set discussed in what follows.

The simplest basis used here is the 6-31+G* basis.[31] This is denoted 6-31G(1). The next basis is again built on the 6-31G *sp* set, but in keeping with the results of our previous work on the need for core-type polarization functions for the alkali atoms, we have augmented the 6-31G basis with the following function types and exponents Li: $p(1.00,0.33)$, $d(0.2)$; Na: $d(1.00,0.175)$; F: $d(1.12,0.32)$ L(0.1076,0.03); Cl: $d(1.05,0.30)$, L(0.0483). This basis is designated as 6-31G(2) below.

The 6-311G basis sets are all based on 6-311G *sp* sets[32] for Li and F, and a (12S9P/6S5P) McLean and Chandler[33] basis for Na. The 6-311G basis set is then augmented with successive diffuse and polarization functions in the following fashion:

(i) 6-311G(1): Li, $p(1.00)$; Na, $d(1.00)$; F, $d(0.8)$ L(0.1076);

(ii) 6-311G(2): Li, $p(1.00,0.33)$; Na, $d(1.00,0.175)$; F, $d(1.12,0.32)$ L(0.1076)

(iii) 6-311G(3): Li, $p(1.00,0.33)$; Na, $d(1.00,0.175)$; F, $d(1.12,0.32)$ L(0.1076,0.0300)

(iv) 6-311G(4): Li, $p(1.00,0.33)$; Na, $d(1.00,0.175)$; F, $d(1.12)f(0.80)$, L(0.1076,0.030)

(v) 6-311G(5): Li, $p(3.00,1.00,0.33)$ $d(2.0,0.5)$; Na, $d(3.00,1.00,0.175)f(3.00,0.75)$; F, $d(3.00,1.12,0.32)$ $f(2.4,0.4)$ L(0.1076,0.0300).

Schematically, the 6-311G(1) basis set augments the 6-311G basis with one set of polarization functions on each atom (appropriate to the core for the alkali atoms) and a set of moderately diffuse functions on F. 6-311G(2) splits all polarization functions on each atom, 6-311G(3) then adds a second diffuse function on F to 6-311G(2). 6-311G(4) adds a single f function to fluorine, while 6-311G(5) adds a third polarization function to each atom, two second polarization functions to Li and Na, and one more second polarization function to fluorine.

In the correlated calculations the $n-1$ shell of each alkali atom was correlated, since it was found important in our previous study of the symmetrical dimers[23] to correlate these electrons for accurate geometries. Thus, in LiF, only the F 1s orbital was treated as core, and in NaF, only the Na and F 1s orbitals were treated as core.

TABLE I. LiF in various basis sets.[a]

Basis set	Method	E_{MX}	R_{LiF}	ω_e
6-31G(1)	SCF	−106.9464	1.575	928
6-31G(1)	MP2	−107.1489	1.588	902
6-31G(1)	CCSD	−107.1477	1.579	922
6-31G(1)	CCSD(T)	−107.1513	1.581	
6-31G(2)	SCF	−106.9506	1.567	932
6-31G(2)	MP2	−107.1858	1.575	947
6-311G(1)	SCF	−106.9772	1.561	935
6-311G(1)	MP2	−106.2113	1.586	880
6-311G(1)	CCSD	−107.2104	1.579	894
6-311G(2)	SCF	−106.9797	1.564	935
6-311G(2)	MP2	−107.2395	1.591	883
6-311G(2)	CCSD	−107.2395	1.583	897
6-311G(3)	SCF	−106.9798	1.564	935
6-311G(3)	MP2	−107.2398	1.591	881
6-311G(3)	CCSD	−107.2397	1.584	896
6-311G(4)	SCF	−106.9828	1.557	941
6-311G(5)	SCF	−106.9842	1.555	941
Slater[b]	SCF		1.554	938
Slater[b]	CISD		1.571	919
	Expt[c]		1.564	910

[a]Bond lengths in Å, energies in hartrees, ω_e in cm^{-1}. See the text for definitions of basis sets.
[b]Results from Langhoff et al. in Ref. 34.
[c]Microwave R_e value quoted in Ref. 35.

III. RESULTS

Since LiNaF_2 is the smallest mixed dimer possible it will be treated here with the widest array of basis sets and methods. While it is not necessarily the case that results obtained for it are transferable to other larger systems, the results do serve as suggestive pointers for the qualitative behavior of the larger dimers. With this in mind the results for the LiF and NaF monomers are presented in Tables I and II as a function of basis set. In many cases we have

TABLE II. NaF in various basis sets.[a]

Basis set	Method	E_{MX}	R_{NaF}	ω_e
6-31G(1)	SCF	−261.3215	1.929	543
6-31G(1)	MP2	−261.5256	1.946	509
6-31G(1)	CCSD	−261.5235	1.936	520
6-31G(1)	CCSD(T)	−261.5273	1.939	···
6-31G(2)	SCF	−261.3253	1.924	554
6-31G(2)	MP2	−261.5916	1.936	538
6-311G(1)	SCF	−261.3561	1.927	541
6-311G(1)	MP2	−261.7237	1.951	513
6-311G(1)	CCSD	−261.7208	1.943	
6-311G(2)	SCF	−261.3603	1.918	554
6-311G(2)	MP2	−261.7525	1.935	530
6-311G(2)	CCSD	−261.7499	1.927	
6-311G(3)	SCF	−261.3605	1.918	554
6-311G(4)	SCF	−261.3630	1.914	554
6-311G(5)	SCF	−261.3659	1.920	549
Slater[b]	SCF		1.923	540
Slater[b]	CISD		1.921	538
	Expt[c]		1.926	536

[a]Bond lengths in Å, energies in hartrees, ω_e in cm^{-1}. See the text for definitions of basis sets.
[b]Results from Langhoff et al. in Ref. 34.
[c]Microwave R_e value quoted in Ref. 35.

performed both uncorrelated and correlated calculations.

All the self-consistent field (SCF) results for the monomer bond lengths agree to within 0.020 Å. The smaller basis sets tend to yield somewhat longer bond lengths than the experimental value, whereas the larger basis sets tend to be a bit shorter than the experimental values. The vibrational frequencies are a bit high, but are similar to those obtained by Langhoff et al.[34] The results due to Langhoff et al.[34] were obtained in a large Slater basis and should be close to the Hartree–Fock limit for the monomers. It is worth noting that in the progression of calculations for NaF one finds that addition of f functions on fluorine causes a reasonably large undershooting of the NaF bond length, and only when one adds f functions to Na (with exponents appropriate to the core orbitals of Na) does the bond length rise again, coming closer to experiment and the results of Langhoff et al.[34]

For both LiF and NaF the inclusion of correlation leads to a small lengthening of the bonds, ~0.01–0.02 Å for both MP2 and CCSD. In the smallest basis set, CCSD(T) leads to a small lengthening relative to CCSD. The MP2 bond lengths are somewhat greater than the CCSD results. For NaF the CCSD and MP2 results come into better agreement with experiment as the basis is augmented, whereas for LiF the agreement becomes somewhat worse as the basis is expanded in those basis sets that we have used at the correlated level. The lengthenings lead to larger bond lengths than experiment, and in some cases give rise to larger errors than the SCF values. However, this is not a major concern, as all methods and basis sets are, in any event, in quite good agreement with experiment for geometries. In addition, it will be shown below that the change in bond length upon dimer formation is insensitive to the monomer bond lengths for all the calculations reported here. If the CCSD bond length increase relative to the HF result were constant as the basis set was expanded, then the LiF lengths in the 6-311G(5) basis would straddle the experimental value. It is, however, of interest to note that the NaF bond length in the smaller basis sets does expand when correlated, whereas the CISD results of Langhoff et al.[34] yields a small decrease in length relative to the SCF value. The MP2 vibrational frequencies undershoot the experimental values, which is likely due in part to the error in the computed geometry which in turn yields inaccurate frequencies.[36]

The 6-31G(2) RHF results for the four dimers considered here are given in Table III. In all cases we sought and found planar rhomboidal stationary points. The planar rhomboidal structure was found to be the lowest energy minimum in the symmetrical dimers. In Ref. 23 we had checked for stability of the linear structures by displacing them slightly from linearity. More recently we have calculated analytical vibrational frequencies for linear Li_2F_2, and while they are quite small, at least at the RHF level, they turn out to be positive for all vibrations. We have not checked the stability at correlated levels. However, the potential is quite flat, and since the linear structures are significantly higher in energy than the rhomboidal species, the rhomboidal structures will be the predominant structures

TABLE III. RHF dimer geometries and binding energies.[a]

	R_{M1X1}	R_{M1X2}	R_{M2X1}	R_{M2X2}	Θ_{X1M1X2}	$E_{binding}$
$LiNaF_2$	1.701	1.701	2.080	2.080	110	63.9
$LiNaCl_2$	2.209	2.209	2.587	2.587	117	48.2
Li_2FCl	1.700	2.245	1.700	2.245	103	57.2
Na_2FCl	2.047	2.589	2.047	2.589	97	54.4

[a]Bond lengths in Å, bond angles in degrees, $E_{binding}$ in kcal/mol. Results are from RHF calculations in the 6-31G(2) basis. The monomer results in this basis set at the RHF level for LiCl and NaCl are, LiCl, $E = -467.0161$ h, $R_e = 2.043$ Å, $\omega_e = 639$ cm^{-1}; NaCl, $E = -621.4051$ h, $R_e = 2.391$ Å, $\omega_e = 354$ cm^{-1}.

at low temperatures, and at high temperatures the linear structures are unlikely to be found as localized structures. Below we treat the possibility of stable linear geometries of $LiNaF_2$ at the RHF level and find two possibilities, both of which have very small, but positive, vibrational frequencies. However, since they are significantly higher in energy than the rhomboidal structure, and since the potential is so flat at the linear geometries, we have not pursued these structures for the other mixed dimers.

In the rhomboidal structures, the dimer bond lengths are quite similar to those obtained previously in our study of the symmetrical dimers.[23] (While the basis sets used in Ref. 23 are slightly different, the results presented below indicate that the changes with basis set modification are small, and that meaningful comparisons between the past results and those presented here are possible.) The bond angles are somewhat different however, as might have been expected. In the mixed dimers containing both Li and Na, the halide–Li–halide angle is ~ 10° larger than for the corresponding symmetrical dimer, whereas the halide–Na–halide angle is 9° smaller for F and 8° smaller for Cl. In the mixed dimers where the two halide atoms are different, the F–M–Cl bond angles are essentially the average of the appropriate two symmetrical values. The binding energies [calculated as $-(E_{dimer} - E_{monomer1} - E_{monomer2})$] are in the range of those found for the symmetrical dimers, although the $LiNaCl_2$ value is somewhat lower than that found for either Li_2Cl_2 or Na_2Cl_2. It should be noted that our previous results[23] indicated that basis set superposition effects had at most a 1 kcal/mol effect on the dimerization energies in a basis set similar to the 6-31G(2) set used here. Since most of those used in the present study are at least as large as this, we expect basis set superposition effects to be minimal here as well at the SCF level, and the constancy of the estimated binding energies at the correlated level (Table V) also suggests it would have a minor effect on those results as well.

The vibrational frequencies for the dimers are presented in Table IV. Based on the results presented below these values are not expected to change drastically (< 10%) with basis set improvement at the RHF level, or upon inclusion of correlation.

In Tables V and VI we present a series of calculations to test the sensitivity of the $LiNaF_2$ results of Tables III and IV to inclusion of correlation and basis set extensions. In general it is found that the bond lengths agree to within

TABLE IV. Dimer vibrational frequencies, RHF.[a]

	A_1	A_1	A_1	B_2	B_2	B_1
LiNaF$_2$	625	400	301	720	343	252
LiNaCl$_2$	399	243	179	519	229	155
Li$_2$FCl	701	489	280	637	377	245
Na$_2$FCl	406	265	176	404	213	132

[a]Vibrational frequencies in cm^{-1}. The molecules are oriented so that the z axis is the rotation axis and the x axis is perpendicular to the molecular plane. Results are from RHF calculations in the 6-31G(2) basis.

TABLE VI. LiNaF$_2$ dimer vibrational frequencies.[a]

Method	Basis	A_1	A_1	A_1	B_2	B_2	B_1
SCF	6-31G(2)	625	400	301	720	343	252
SCF	6-311G(1)	627	394	302	711	337	257
MP2	6-311G(1)	592	374	290	672	322	246
SCF	6-311G(2)	628	400	303	719	342	253
SCF	6-311G(3)	628	399	302	719	341	252
SCF	6-311G(4)	628	399	301	717	338	252
SCF	6-311G(5)	627	396	300	719	338	252

[a]Vibrational frequencies in cm^{-1}. The molecular orientation is that of Table IV.

0.02 Å for all methods and basis sets, the bond length expansions upon dimerization agree to within 0.015 Å, the bond angle is predicted to be 109°–110°, and the dimerization energy is ~62–63 kcal/mol. It is also seen that CCSD and CCSD(T) yield essentially equal dimerization energies. This modest effect of triple excitations on the bond strength of the dimer is largely due to the fact that the bonding is principally ionic, and reactants and products are closed shell species. The vibrational frequencies are insensitive to basis set expansion at the RHF level. Correlation alters the monomer frequencies to some extent, but does not lower them the usual 9%–11%, but instead has about a 5%–6% effect[34] on the LiF frequency, and an even smaller effect on the NaF frequency. Since the bonding is similarly ionic in the dimer we again expect little effect on the dimer frequencies upon correlation (see Tables V and VI). To test this we performed frequency calculations at the MP2 level in the 6-311G(1) basis set for LiNaF$_2$. The MP2 vibrational frequencies are below, but are still reasonably close to the RHF values. Given the monomer results reported above one expects that MP2 likely underestimates the actual values, while the SCF results are slight overestimates.

In recent experiments and associated theoretical results on LiNaF$_2$, tentative assignments were made to bands of metastable linear forms of the molecule. To obtain information on these linear species RHF calculations in the 6-311G(1) basis set were performed. In both cases we find the molecules to have seven positive vibrational frequen-

TABLE V. LiNaF$_2$ geometries and binding energies.[a]

Basis	Method	R_{LiF}	ΔR_{LiF}	R_{NaF}	ΔR_{NaF}	Θ_{FLiF}	$E_{binding}$
6-31G(1)	SCF	1.702	0.128	2.085	0.156	110	64.2
6-31G(1)	CCSD	1.693	0.114	2.100	0.165	112	65.1
6-31G(1)	CCSD(T)	1.695	0.114	2.103	0.165	112	65.0
6-31G(2)	SCF	1.701	0.134	2.080	0.156	110	63.0
6-31G(2)	MP2	1.710	0.136	2.080	0.144	110	62.9
6-311G(1)	SCF	1.699	0.138	2.082	0.156	109	63.9
6-311G(1)	MP2	1.728	0.142	2.107	0.156	109	61.9
6-311G(1)	CCSD	1.719	0.140	2.098	0.155	109	63.0
6-311G(2)	SCF	1.700	0.137	2.073	0.155	110	63.2
6-311G(2)	MP2	1.730	0.139	2.088	0.153	110	61.6
6-311G(2)	CCSD	1.720	0.137	2.079	0.152	110	62.8
6-311G(3)	SCF	1.700	0.136	2.074	0.156	110	63.2
6-311G(4)	SCF	1.694	0.137	2.073	0.159	110	62.4
6-311G(5)	SCF	1.692	0.137	2.078	0.158	110	62.4

[a]Bond lengths and bond length changes in Å, bond angles in degrees, $E_{binding}$ in kcal/mol.

cies, indicating that at this level of theory, the linear structure is a minimum. The energies, geometries, and frequencies at this level of calculation are (a) Li–F–Na–F: $E= -368.377\ 87$ h, $R_{LiF}=1.594$ Å, $R_{NaF,central}=2.126$ Å, $R_{NaF} =1.968$ Å, $\omega^{\pi}=21.2$ cm^{-1}, $\omega^{\pi}=126.5$ cm^{-1}, $\omega^{\sigma}=252.3$ cm^{-1}, $\omega^{\sigma}=513.5$ cm^{-1}, $\omega^{\sigma}=866.9$ cm^{-1}, $E_{binding}=28.0$ kcal/mol. (b) Na–F–Li–F: $E=-368.399\ 29$ h, $R_{NaF} =1.960$ Å, $R_{LiF,central}=1.742$ Å, $R_{LiF}=1.621$ Å, $\omega^{\pi}=14.3$ cm^{-1}, $\omega^{\pi}=218.3$ cm^{-1}, $\omega^{\sigma}=275.1$ cm^{-1}, $\omega^{\sigma}=543.4$ cm^{-1}, $\omega^{\sigma}=921.0$ cm^{-1}, $E_{binding}=41.4$ kcal/mol. Of course, the bending frequencies are quite small and it is entirely possible that upon correlation or basis set augmentation these structures could become unstable [the Na–F–Li–F structure has two imaginary frequencies at the RHF level in the 6-31G(1) basis] but it is clear that these species will most likely only be observed in matrix environments.

IV. DISCUSSION

The experimental monomer bond lengths and vibrational frequencies are not in doubt.[35] Thus, the main purpose for comparing our results to the experimental values is to obtain error bars for the dimer results. At the 6-31G(2), where all four dimers were treated, we find that the RHF monomer bond lengths are within 0.003 Å of experiment for LiF and NaF and within 0.03 Å for LiCl and NaCl. The excellent agreement for the fluorides even in the small basis sets is somewhat fortuitous, as basis set expansion tends to decrease the bond length, while correlation tends to increase it. For the chlorides the errors are somewhat larger, and we expect similar absolute errors to be carried over to the dimers. The vibrational frequencies for the monomers are all within 3%–4% of the experimental value at the RHF level. The MP2 bond lengths, especially in the smaller basis sets tend to be too long, and the vibrational frequencies are too low. CCSD yields bond lengths that are too long as well, but do not overshoot as much as the MP2 results. To the extent that we have performed the calculations, we find no significant improvement with basis set for CCSD or MP2 for R_e for LiF, but modest improvement in ω_e. CCSD and MP2 both yield improved estimates of R_e and MP2 yields an improved ω_e for NaF as the basis set is improved, however.

As might have been expected, a large body of ab initio work has appeared for the monomers.[24,25,34,37–40] The present results are quite comparable to the larger calcula-

tions reported in the literature. One interesting difference in the literature results is found in the bond length of NaF. The CISD results of Langhoff et al.[34] predict a modest bond-length contraction relative to the SCF value, whereas more recent two-reference perturbation theory selected CISD calculations in fairly large Gaussian basis sets find a bond-length expansion relative to the RHF value. In our case, we find an expansion at the MP2 and CCSD levels in the 6-311G(1) and 6-311G(2) basis sets.

In forming the dimers the major change that occurs is the individual M–X bonds increase relative to their monomer values. This has been observed previously for various symmetrical dimers.[1-8,23-26] The bond length expansions appear to be similar to those found in the symmetrical dimers, with some minor changes in LiF and NaCl. In the 6-31G(2) basis at the RHF level the LiF expansion is ~0.135±0.001 Å, LiCl: 0.185±0.02 Å, NaF: 0.140 ±0.015 Å, and NaCl: 0.197±0.001 Å, compared to the symmetrical dimers at the RHF level in the basis set of Ref. 23 which are 0.152, 0.181, 0.142, and 0.174 Å, respectively. We again note that inclusion of correlation has a relatively modest effect on the bond length expansions.[23]

Relatively little *ab initio* work has appeared for clusters of alkali halides, and that which is available has been concerned exclusively with symmetrical dimers and higher clusters.[23-26] Direct comparison is thus not possible, but it was found in Ref. 23 that calculations similar to those reported here were in quite good agreement with the other theoretical results on the symmetrical dimers.

From the series of calculations on $LiNaF_2$ it appears that one will draw similar conclusions no matter which level of calculation is used to compare with experiment. That being the case the 6-311G(2) basis will be used in the comparisons made below, since it is the largest basis for which CCSD results for geometries and energies were obtained for the dimer. The earliest experimental results to our knowledge obtained for $LiNaF_2$ are those of Cyvin et al.[21] They examined IR spectra of matrix isolated alkali halide species produced from vapors over mixtures of NaF and LiF. They reported assignments of bands at 660 and 376 cm^{-1} for two of the three A_1 modes (one of the modes was not observed, but was estimated to occur at 321 cm^{-1}), 589 and 326 cm^{-1} for the B_2 modes, and 238 cm^{-1} for the B_1 mode. The pattern is similar to that found here, but requires that the SCF results be too high by on the order of 10% in most cases. While that is possible, the MP2 frequencies support a more modest alteration of the frequencies upon correlation, as do the monomer results of Ref. 34.

More recently, Ramondo et al.[22(a)] used matrix isolation techniques (Ar matrix) and FTIR spectroscopy to examine the mixed dimer $LiNaF_2$. A polarizable ion model[22(b)] was used in concert with the experiments to sort out the various observed lines. They assigned vibrational peaks at 708 and 362 cm^{-1} as B_2 modes, 580–590 and 371 cm^{-1} as A_1 modes, and 233 cm^{-1} as a B_1 mode. These results are somewhat closer to the present theoretical results. One notes that there is some discrepancy as to the choice of the highest A_1 and B_2 modes when compared

with the Cyvin et al.[21] data. Our results concur with the assignment of Ramondo et al.[22(a)] In comparison with the model calculations by Ramondo et al.[22(a)] it is found that their LiF and NaF bond lengths are significantly longer than those reported here by from 0.03/0.05 Å (LiF:CCSD/SCF) to 0.05/0.07 Å (NaF:CCSD/SCF). In our past study we noted that semiempirical models show wide variability in which parameters are predicted most accurately. Given the insensitivity of the $LiNaF_2$ results to basis set extensions or correlation inclusion, it would seem that the present results are more near the actual experimental geometry. In comparison with their assignments[22(a)] for linear structures of $LiNaF_2$ we get relatively poor agreement. Our results do agree with their relative ordering of LiF and NaF frequencies between the two different forms of the linear dimer, but our frequencies are significantly higher than theirs, especially for the LiF stretch frequencies.

Finally, it should be noted that the $LiNaF_2$ calculations strongly suggest that larger clusters of the fluorides can be examined with relatively modest basis sets at the RHF level with reasonable accuracy. This statement has not been exhaustively checked but we are in the process of examining larger LiF clusters[41] and others have seen similar regularity in NaCl clusters.[26] While this does not mean that *ab initio* results for 100 atom clusters are on the doorstep, it does suggest that at least for LiF and NaF one might use a succession of *ab initio* cluster results to develop more reliable semiempirical models, and then utilize the improved model to explore very large clusters. Work is underway in this direction for LiF presently.[41]

V. CONCLUSIONS

Results for ground state geometries, vibrational frequencies, and dimerization energies of a series of mixed alkali halide dimers have been presented based on *ab initio* RHF, MP2, and CCSD wave functions. The mixed dimers have been shown to be quite similar to the symmetrical dimers, the largest changes relative to the symmetrical dimers arising in the dimer bond angles. Experimental vibrational assignments appear to only have been made for the mixed dimer $LiNaF_2$, and in this case the present RHF results are somewhat high, but in reasonable agreement. It is found that basis set extensions have only a modest effect on the computed geometries and frequencies, and that while correlation tends to increase the monomer and dimer bond lengths, it has a much smaller effect on the dimer bond angles and the estimated bond length expansion upon dimer formation. The results suggest that larger clusters can be studied using relatively modest available *ab initio* methods.

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