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Equilibrium Gas-Phase Structures of Sodium Fluoride, Bromide and Iodide Monomers and Dimers

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ABSTRACT: The alkali halides sodium fluoride, sodium bromide and sodium iodide exist in the gas phase as both monomer and dimer species. A reanalysis of gas electron diffraction (GED) data collected earlier has been undertaken for each of these molecules using the EXPRESS method to yield experimental equilibrium structures. EXPRESS allows amplitudes of vibration to be estimated and corrections terms to be applied to each pair of atoms in the refinement model. These quantities are calculated from the *ab initio* potential-energy surfaces corresponding to the vibrational modes of the monomer and dimer. Because they include many of the effects associated with large-amplitude modes of vibration and anharmonicity we have been able to determine highly accurate experimental structures. These results are found to be in good agreement with those from high-level core-valence *ab initio* calculations and are substantially more precise than those obtained in previous structural studies.

KEYWORDS: electron diffraction – alkali halide – structural chemistry – equilibrium structure

■ INTRODUCTION

Gas-phase experimental structures provide the ideal comparison with the growing number of structures calculated *ab initio*. However, care must be taken when comparing results obtained from experimental and theoretical methods as they determine different distances. As experimental data are the ultimate check of the reliability of theoretical studies, these subtle effects must be addressed.

A computed geometry, the so-called equilibrium structure (r_e), corresponds to a hypothetical motionless molecule at a minimum of the Born-Oppenheimer potential-energy surface. This is hypothetical as real molecules are never motionless, even at 0 K. Experimental structures have a physical meaning, which depends on the nature of the experiment used to determine them. X-ray diffraction, for example, measures the centers of electron density, whereas electron and neutron diffraction studies provide information yielding internuclear distances. The way the actual vibrational motion is averaged also has an effect on the final structure; this makes direct comparison with theory troublesome. The operational parameter (r_a) yielded by electron diffraction (as a result of the scattering equations, including quantum mechanical vibrational averaging) can be converted to something approaching an equilibrium structure by a traditional multi-step correction process.[1,2] However, in many cases, especially when considering floppy molecules, this correction process can introduce errors larger than those they were supposed to correct.

Alkali halides certainly fall into this category, providing an interesting area of study for the recently developed EXPRESS method (EXPeriments Resulting in Equilibrium StructureS),[3] which calculates accurate vibrational correction terms. The initial test case for this method (sodium chloride) yielded extremely accurate equilibrium structures for both monomer and dimer, which for the first time gave good agreement with high-level *ab initio* results.[3]

Despite the experimental complexities of very low vapor pressures, and thus the need for extremely high temperatures, the gas-phase structures of the alkali halides have been favorite topics for research since the first electron-diffraction experiments in the 1930s.[4] The vapors are generally dominated by the monomer species, and the visual analysis of these first data was judged consistent with a diatomic model, although the resulting distances were somewhat long. Since the early days, the study of these simple textbook molecules has provided fruitful ground for fundamental questions of chemical structure, bonding, and reactivity. During the 1950s the existence of clusters in the vapor phase was first identified through the use of mass spectrometry[5] and molecular beam magnetic resonance experiments.[6,7] In the majority of cases only the monomer (MX) and dimer (M_2X_2) were detected in abundances greater than 1%, with the exception of some of the lithium halides, which can contain small amounts of trimer. Trimers and larger clusters have been observed with sensitive mass spectrometers at the 0.1–0.01% levels for several other alkali halides.[6,7] The first theoretical structures (planar, D_{2h}) of the dimer molecules were proposed in 1955,[8] followed by various models to predict the energies of formation and vibrational frequencies.[9–11] This sparked further electron-diffraction studies in Russia, using Indian ink to protect the photographic plates from the light from the red-hot nozzle,[12,13] as well as a study in the USA by Bauer *et al.*.[14] Microwave techniques, developed around this time, were able to provide accurate information on the predominant monomer (MX) species, but the planar dimers (M_2X_2) could not be studied in this way as they have no dipole moment. Further diffraction studies were attempted[15] and additional models were developed (see Reference 16 for an overview) to determine the structures of these compounds. Because of the experimental complexities, the completion of all the gas-phase structures of the alkali halides was not achieved until the mid-1980s.[1,19] Since then interest in these molecules has remained high and more recently experimental studies have determined the structures of mixed dimers[20,21] in addition to radio-frequency (RF) molecular beam studies of the hyperfine structure of almost all of the alkali halide diatomics, including RbI,[22] NaF,[23] and RbCl.[24] Further microwave studies of monomers have yielded rotational constants of higher accuracy for the purpose of detecting alkali halides in space,[25] and KBr and KI have been studied quite recently using both molecular beam RF[26] and Fourier transform microwave and rotational spectroscopy.[27] Matrix isolation studies of the vibrational frequencies of Cs_2Br_2 and Cs_2I_2 have also been recently published.[28] The literature is peppered with many theoretical studies[16,29–33] which have some difficulty in reproducing the highly accurate microwave monomer distances.

The success of the EXPRESS method (applied to sodium chloride)[3] in providing accurate vibrational corrections has allowed the direct comparison of new high-level *ab initio* calculations and the reanalyzed experimentally-determined structure, achieving good agreement. Following this success, it was proposed that the rest of the sodium halides would also benefit from such a rigorous treatment.

■ EXPERIMENTAL SECTION

Computational Studies. The previous work on sodium chloride[3] demonstrated that relatively accurate geometries could be obtained by using the MP2[33–37] method with core-valence basis sets, correlating all electrons [MP2(full)]. The most accurate results were obtained employing the core-valence basis set of Martin *et al.*[38] for the sodium atom and the equivalent basis set by Dunning[39,40] for the chlorine atom. These basis sets allow for higher orders of angular momentum in the traditional ‘core’ region, which is required when more than just the standard valence electrons are used in the correlation scheme.[41] The calculations reported in this work were mainly performed using the Gaussian 03 suite of programs,[42] making use of machines provided by the EPSRC National Service for Computational Chemistry Software (URL:

http://www.nsccs.ac.uk) and also the facilities of the EaStCHEM Research Computing Facility (http://www.eastchem.ac.uk/rcf). This is partially supported by the eDIKT initiative (http://www.edikt.org). Additional calculations were performed using MOLPRO 2012.1[43] running on hardware at the Center for Advanced Scientific Computing and Modeling (CASCaM) at the University of North Texas. Geometry optimizations were carried out on both the monomer (NaX) and the dimer (Na_2X_2) species for all the sodium halides studied using CCSD(T)/aug-cc-pwCVQZ.[38–40] For the sodium iodide monomer potential curves (11 points spaced 2 pm around the Huber-Herzberg distance) were calculated at the CCSD(T) level with aug-cc-pwCVTZ and aug-cc-pwCVQZ basis sets, as well as extrapolated point-by-point to the basis set limit (using the "W1" recipe).[44] The (2s2p3s) electrons on Na and (4d5s5p) electrons on I were correlated. The sodium iodide dimer geometry was calculated using CCSD(T)/aug-cc-pwCVQZ with the 4d orbitals on I and the (2s2p) orbitals on Na correlated.

The EXPRESS method[3] of exploring the normal vibrational modes was performed at the MP2(full)/6-311+G(d)[45,46] level for sodium fluoride and sodium bromide. Calculations at this level for sodium iodide proved too computationally expensive, so the correlation was restricted to electrons in the two outermost shells [MP2(FC1)]. This restriction has only a small effect on the equilibrium geometry of the sodium iodide monomer or dimer. For all of the calculations the convergence criteria were tightened to 1.236 pN, 0.741 pN, 3.175 fm, and 2.117 fm for the maximum force, root-mean-square force, maximum displacement and root-mean-square displacement, respectively, in order to ensure that consistency was maintained between the energies calculated by the geometry optimization scheme and those calculated while exploring the normal modes using the EXPRESS method.

As in the case of sodium chloride[3] the z axis was defined as passing through the center of the dimer, perpendicular to the plane of the molecule, and the x axis through the two metal atoms. The monomer (MX) has only one mode of vibration, which is of the A_1 symmetry species, and the dimer has six modes of five different symmetry species (stretching: A_g, B_{1g}, B_{2u}, B_{3u}; and bending: A_g and B_{1u}). The vibrational modes were modeled in an identical fashion to those for sodium chloride,[3] with a chosen geometric parameter (ρ) fixed through a series of geometry optimizations and everything else allowed to relax. The EXPRESS method was utilized to calculate the root-mean-square (RMS) amplitudes of vibration (u) and explicit distance corrections ($r_a - r_e$) for each of the three sodium halide dimers and monomers studied at the temperatures used to obtain the experimental data. For a detailed explanation of the EXPRESS method refer to Reference 3.

Gas Electron Diffraction. The data used for this study were those obtained for sodium fluoride at 1123 K,[18] sodium bromide at 920 K,[17] and sodium iodide at 848 K[19] by Hartley *et al.* using the technique identical to that used for the study of the alkali chlorides.[1] High-purity, commercially available samples were used (purity > 99.97%). Accelerating voltages of around 40 keV were used and the precise electron wavelengths were determined using the standard r_a(C−O) value for CO_2 of 116.42 pm.[48,49] The scattering intensities were determined by counting electrons at each angle for 300 s. These were then averaged at intervals of 2 nm^{-1}. For sodium fluoride the averaged data were unavailable and so the raw experimental data were used and re-averaged at intervals of 1 nm^{-1} (which is now our current standard for runs at these nozzle-to-detector distances).

The weighting points for the off-diagonal weight matrix, correlation parameters and scale factors for the data are given in Table S1. Further data reduction and the least-squares refinements were then carried out using the ed@ed v2.4 refinement program[49] using the scattering factors of Ross *et al.*.[50]

As is generally the case in electron diffraction studies, inelastic scattering was not included explicitly on the basis that it is typically non-oscillatory (especially at wider scattering angles) and is, therefore, removed with the background in this kind of analysis.

The electron diffraction data were modeled using standard two-atom scattering equations. Quantitatively predicting the effects of three-atom scattering on the geometries of the species presented is difficult because of the correlation that exists between parameters. The very reasonable agreement with theory of these corrected equilibrium structures indicates that the two-atom scattering model is adequate here.

■ RESULTS AND DISCUSSION

Computational Studies. Previous work on sodium chloride[3] has shown that the choice of basis set is vital to reproduce the accurate microwave results effectively for the monomer (NaCl) using theoretical calculations. Calculations were performed for sodium bromide, the results of which are shown in Table 1 together with other prominent results from the literature.

Table 1. Calculated Geometries (r_e) for the Sodium Bromide Monomer and Dimer at Different Levels of Theory[a]

theory / basis set	r_e(Na–Br)$_m$	r_e(Na–Br)$_d$	$\angle_e$(Br–Na–Br)	Δr_e(Na–Br)
CCSD(T)/aug-cc-pwCVQZ[b]	250.8	268.2	104.2	17.4
CCSD(T)/aug-cc-pwCVQZ[c]	—	268.2	104.2	—
RHF/ECP[d]	256.9	277.0	103.9	20.1
MP2/POL-ECP[e]	253.4	271.3	104.0	17.9
DFT/TZP[f]	247.3	264.4	105.2	17.1
Born-Mayer potential[g]	—	281.3	105.7	—
Harrison potential[g]	—	276.8	108.2	—
Shell Model[h]	248	269	102	21
expt. (MW)[i]	250.2	—	—	—

[a] Distances in pm, angles in degrees. m denotes monomer and d denotes dimer. [b] Calculations included correlation for orbitals 3s3p3d on Br and 2s2p on Na. [c] As for *b* but with the 3s3p orbitals on Br frozen. [d] Wetzel *et al.*[32] [e] Törring *et al.*[16] [f] Modisette *et al.*[30] [g] Chauhan *et al.*[51] [h] Welch *et al.*[52] [i] Brumer *et al.*[53]

Utilizing the core-valence basis sets developed by Dunning *et al.* for bromine[39,40] and the corresponding one by Martin *et al.* for sodium,[38] together with the CCSD(T) method the theoretical results for the monomer could be brought to within 0.6 pm of the experimental value. By performing calculations with different orbital correlations we have been able to deduce that the halogen (*N*–1)d correlation is crucial for the accuracy of this work, while correlating (*N*–1)s(*N*–1)p is less critical.

Results from the literature shown in Table 1 also show that the inclusion of electron correlation has the effect of shortening the sodium-bromine bond. The DFT results underestimate the monomer value when compared with the microwave value.

Having firmly established the need for core correlation and appropriate core-valence basis sets to calculate the structures of both sodium chloride and sodium bromide accurately the same could be assumed for the other sodium halides (NaF and NaI). The results of calculations performed on sodium fluoride are listed in Table 2 together with other prominent results from the literature.

Table 2. Calculated Geometries (r_e) for Sodium Fluoride Monomer and Dimer at Different Levels of Theory[a]

theory / basis set	r_e(Na–F)$_m$	r_e(Na–F)$_d$	$\angle_e$(F–Na–F)	Δr_e(Na–F)
CCSD(T)/aug-cc-pwCVQZ	192.9	206.7	93.9	13.8
RHF/STO[b]	192.3	—	—	—
RHF/POL[c]	192.3	206.5	93.1	14.2
MP2/POL[c]	194.2	209.4	92.9	15.2
MP2/modDUN[d]	198.2	214.1	88.7	15.9
CI(SD)/STO[d]	192.1	—	—	—
CCSD(T, all)/CV5Z[e]	192.8	—	—	—
DFT/TZP[f]	191.6	204.7	94.8	13.1
Born-Mayer potential[g]	—	209.4	90.8	—
Harrison potential[g]	—	204.5	94.7	—
Shell model[h]	161	190	89	29
Expt. (MW)[i]	192.6	—	—	—

[a] Distances in pm, angles in degrees. [b] Langhoff *et al.*[54] [c] Dickey *et al.*[55] [d] Lintuluoto[56] [e] Iron *et al.*[38] [f] Modisette *et al.*[30] [g] Chauhan *et al.*[51] [h] Welch *et al.*[52] [i] Brumer *et al.*[53]

For sodium fluoride our very high level calculations reproduce the monomer distance to within 0.3 pm of the value from rotational spectroscopy. It is notable that results from the literature using specifically developed basis sets reproduce the experimental monomer distance remarkably well (also within 0.3 pm) simply using spin-restricted Hartree-Fock (RHF).[55] However, calculations using the same basis set but including electron correlation on valence electrons at the MP2 level did not fare so well, overcalculating the monomer distance by 1.6 pm. As is often the case, the success of the RHF calculations is somewhat fortuitous. Other calculations using MP2 theory also overestimate the monomer distance, this time by 5.6 pm. The CCSD(T) calculation of Iron *et al.* provides the best result, being only 0.2 pm away from the experimental value. DFT once again underestimates the monomer bonded distance. Despite the wide range of absolute values the monomer to dimer lengthening again remains reasonably constant (ranging from 13.1 to 15.9 pm) throughout the calculations.

The results of calculations of the equilibrium structure of the monomer and dimer of sodium iodide are detailed in Table 3, together with a selection of literature values. These show that the only method that comes close to predicting the experimental monomer bond length of 271.1 pm is the CCSD(T)/aug-cc-pwCVQZ calculation. All of the comparably large calculations for the sodium halides, including NaCl,[3] find a monomer distance that is slightly longer than the microwave value, indicating that possible relativistic effects for heavier atoms such as Br and I apparently do not play a major role in these ionic bonds.

Table 3. Calculated Geometries (r_e) for Sodium Iodide Monomer and Dimer at Different Levels of Theory[a]

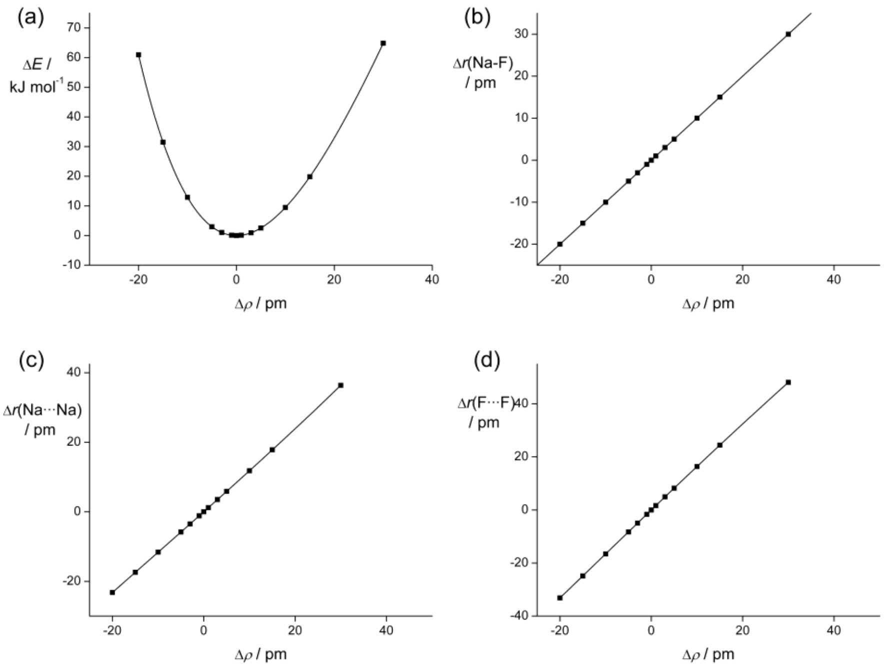
Theory / basis set	r_e(Na–I)$_m$	r_e(Na–I)$_d$	$\angle_e$(I–Na–I)	Δr_e(Na–I)
CCSD(T)/aug-cc-pwCVTZ[b]	273.9	291.9	107.5	18.0
CCSD(T)/aug-cc-pwCVQZ[c]	272.1	290.7	107.3	18.6
RHF/ECP[d]	277.7	299	107.4	21.3
MP2/POL-ECP[e]	273.7	291.9	107.5	18.2
Born-Mayer potential[f]	—	268.6	108.2	—
Harrison potential[f]	—	257.4	112.0	—
Shell model[g]	263	287	105	24
Expt. (MW)[h]	271.1	—	—	—

[a] Distances in pm, angles in degrees. [b] Dimer values are from a CVTZ val+4s4p4d calculation. [c] Dimer values are from a calculation including correlation for orbitals 4d on I and 2s2p on Na. [d] Wetzel *et al.*[32] [e] Törring *et al.*[16] [f] Chauhan *et al.*[51] [g] Welch *et al.*[52] [h] Brumer *et al.*[53]

Harmonic force fields were calculated at the MP2(full)/6-311+G(d) level for both sodium fluoride and sodium bromide, and at the MP2(FC1)/6-311+G(d) level for sodium iodide. These were used to calculate vibrational correction terms using traditional methods for comparison with the EXPRESS method. The vibrational frequencies for the monomers and the six vibrational frequencies for the dimers are shown in Table S2, together with experimental values.

Potential-energy curves for all modes of vibration together with variations in interatomic distances were calculated for each of sodium fluoride, sodium bromide and sodium iodide. One example is shown in Figure 1 and all others are available in Supplementary Information in Figures S1–S6 for sodium fluoride, Figures S7–S13 for sodium bromide, and Figures S14–S20 for sodium iodide, respectively. Here all vibrational coordinates and parameters are the same as those defined in Reference 1.

Figure 1. Plots of changes in (a) total energy, (b) r(Na–F) bonded distance, (c) r(Na···Na) non-bonded distance and (d) r(F···F) non-bonded distance against change in vibrational mode parameter (ρ) for the A_g stretching motion of the Na_2F_2 dimer.



These potential functions and distance variations were then used to calculate the RMS amplitudes of vibration (u^m) and distance correction terms [$(r_a - r_e)^m$] using the EXPRESS method, which is described in full detail elsewhere.[3] As an example, Table 4 shows the explicitly calculated RMS amplitudes of vibration (u^m) for each mode of the monomer and dimer, together with the corresponding distance corrections [$(r_a - r_e)^m$], for sodium fluoride; the corresponding tables for sodium bromide and sodium iodide are in Supplementary Information (Tables S3 and S4), respectively. Also shown are the overall RMS amplitudes of vibration (u) and distance corrections ($r_a - r_e$) for each distance, calculated as described above, and the centrifugal distortion terms (δr) calculated using SHRINK.[58,59] Although the monomer u values are uniformly larger than those calculated using the harmonic formula[1] and the experimental vibrational frequencies, the resulting monomer ($r_a - r_e$) values and overall ($r_a - r_e$) + δr distance corrections agree with the earlier formula values to within a few percent.[17–19]

Table 4. RMS Amplitudes of Vibration (u) and Distance Corrections ($r_a - r_e$) for NaF and Na_2F_2 Computed using the EXPRESS Method at 1123 K, Centrifugal Distortion Corrections (δr) and Overall $r_a - r_e$ Corrections[a]

distance		A_1 stretch	A_g stretch	B_{1g} stretch	B_{2u} stretch	B_{3u} stretch	A_g Bend	B_{1u} bend	Total	δr [b]	overall $(r_a - r_e) + \delta r$
monomer											
Na–F	u	10.67							10.67		
	$r_a - r_e$	1.81							1.81	0.98	2.79
Dimer											
Na–F	u		6.74	8.17	7.39	7.25	0.52	0.60	14.83		
	$r_a - r_e$		0.79	1.00	0.80	0.85	0.18	0.33	3.05	0.60	3.65
Na···Na	u		7.93	3.14	3.42	0.62	16.45	2.01	18.96		
	$r_a - r_e$		1.00	1.74	1.93	0.34	−1.34	−1.21	2.46	0.92	3.38
F···F	u		11.06	4.07	1.29	4.07	16.83	2.14	21.09		
	$r_a - r_e$		1.21	2.26	0.73	2.34	−0.96	−1.27	4.31	0.78	5.09

[a] All values are in pm. [b] Calculated from MP2(full)/6-311+G(d) harmonic force field using SHRINK.[58,59]

For all three of the dimer molecules the RMS amplitudes of vibration corresponding to the bonded distances (Na–X) are made up predominantly from the contributions of the four stretching motions (A_g, B_{1g}, B_{2u}, B_{3u}). The RMS amplitudes of vibration for the non-bonded distances (Na···Na and X···X) are derived predominantly from the A_g stretching and the A_g bending motions, with small but significant contributions from the B_{1u} out-of-plane (oop) bending motions. As expected, the size of the RMS amplitudes of vibration and distance corrections ($r_a - r_e$) increase through the series of increasing molecular weight as the force constants relating to the traditional normal modes of vibration decrease.

Particular attention must be paid to the out-of-plane B_{1u} bending motion (Figures S6, S13 and S20 for Na_2F_2, Na_2Br_2 and Na_2I_2, respectively), as this best illustrates the ability of the EXPRESS method to capture accurately the true nature of the vibrational motions. It can be seen from these figures that as the dimer molecules bend the Na–X bonds lengthen. This can be interpreted as a coupling with the A_g stretching mode. This is possible because, as the molecules bend out of the plane (B_{1u}), the overall symmetry drops from D_{2h} to C_{2v}. Thus, both the A_g stretch and B_{1u} bend take on A_1 symmetry and therefore can couple. The ability of the EXPRESS method to capture this sophisticated behavior is in marked contrast to traditional methods, such as the detailed earlier study of Na_2Cl_2.[60]

Comparison of the overall amplitudes of vibration and distance corrections obtained by this method and the equivalent values from previous approaches are shown in Table 5 for sodium fluoride and in Tables S5 and S6 for sodium bromide and sodium iodide, respectively. All of the traditional approaches are based upon the use of harmonic force fields. The r_{h0} approach corrects for vibrational effects using these harmonic force fields and approximates vibrational motion by computing rectilinear (zeroth-order) corrections. (This can be done using the ASYM program.[61]) The r_{h1} approach is similar but approximates vibrational motion using more sophisticated curvilinear (first-order) corrections. (This can be done using the SHRINK program.[58,59,62,63]) The $r_{a3t,1}$ approach approximates anharmonicity (at a cubic level) by introducing anharmonic effects through the use of tabulated constants. The $r_{a3,1}$ approach takes this one step further and includes anharmonicity (again only at a cubic level) by utilizing anharmonic constants calculated by taking third derivatives with respect to energy. For the out-of-plane bending discussed above the inclusion of a cubic term will make no difference, rather the quartic term would be required. The EXPRESS approach can essentially model anharmonic effects and vibrational motion to any order as this simply depends on the functional form used to fit the potential-energy slices and distance variations.

Table 5. RMS Amplitudes of Vibration and Distance Corrections for NaF and Na_2F_2 at 1123 K[a]

distance		ASYM (r_{h0})[b]	SHRINK (r_{h1})[c]	SHRINK ($r_{a3t,1}$)[d]	SHRINK ($r_{a3,1}$)[e]	EXPRESS (r_e)
monomer						
Na–F	u	9.99	9.99	9.99	9.99	10.67
	$r_a - r_x$	0.47	0.47	2.90	2.77	2.79
dimer						
Na–F	u	13.76	13.76	13.76	13.76	14.83
	$r_a - r_x$	1.54	0.23	3.33	4.78	3.65
Na···Na	u	19.40	19.46	19.46	19.46	18.96
	$r_a - r_x$	−0.22	−2.23	1.39	3.25	3.38
F···F	u	20.00	20.05	20.05	20.05	21.09
	$r_a - r_x$	−0.33	−2.01	3.11	5.31	5.09

[a] All values are in pm. [b] Obtained from a harmonic force field at MP2(full)/6-311+G(d) level using first-order distance corrections and centrifugal distortion term (δr). [c] As in footnote [b] but using first-order distance corrections. [d] As in footnote [c] but also including cubic anharmonic effects generated from averaged tabulated values. [e] As in footnote [c] but including cubic anharmonic effects generated using third derivatives of the energy.

GED Refinement. The structural refinements of the structures of the sodium halides endeavored to make use of all available experimental data. The GED data provided information on both the monomers (NaX) and the dimers (Na_2X_2) and microwave spectroscopy provided very accurate structural information for the monomer only. The microwave information was introduced into the refinement process in the form of B_e rotational constants employing the SARACEN method.[64–66] SARACEN restraints were also applied to amplitudes of vibration that could not refine independently and also to the ratios of the RMS amplitudes of vibration for monomer and dimer bonded distances. Four independent parameters were used to describe the geometries of the monomer and dimer and the composition of the vapor in each of the refinements. Parameter p_1 describes the monomer bond length r(Na–X), p_2 the dimer bond length r(Na–X), p_3 is the halogen-sodium-halogen angle $\angle$(X–Na–X), and p_4 is the proportion of NaX units existing as dimer in vapor (F_d) as given by

$$F_d = \frac{2m_d}{m_m + 2m_d}, \qquad (1)$$

where m_m and m_d are the relative numbers of moles of monomers and dimers, respectively.

As well as the four parameters the RMS amplitudes of vibration were refined. As the monomer and dimer bonded distances cannot be resolved, the ratios of their RMS amplitudes of vibration were restrained to the values calculated by the EXPRESS method with an associated uncertainty, using the SARACEN method. Any amplitudes that would not refine sensibly were again subject to SARACEN restraints. The starting values for all the RMS amplitudes of vibration were taken from those calculated using the EXPRESS method. For sodium fluoride the refinement parameters, their final values, and all the flexible restraints are shown in Table 6. The refined amplitudes and associated r_a distances are shown in Table S7. The corresponding information for sodium bromide and sodium iodide is shown in Tables 7 and S8, and Tables 8 and S9, respectively.

Table 6. Refined r_e Structures and Composition for NaF Vapor at 1123 K Using the EXPRESS Analysis for Vibrational Corrections[a]

		r_e (expt.)	r_e (theory)[b]	Restraint
independent				
p_1	r(Na–F)$_m$	192.5942(2)	192.9	—
p_2	r(Na–F)$_d$	207.3(4)	206.7	—
p_3	∠FNaF	92.8(6)	93.9	—
p_4	F_d	0.20(2)	—	—
dependent				
d_1	r(Na···Na)	285.9(13)	285.1	—
d_2	r(F···F)	300.4(18)	299.4	—
d_3	Δr(Na–F)[c]	14.7(4)	13.8	—
d_4	B_e ^{23}Na^{19}F	13098.0319(28)	—	13098.0320(30)

[a] Distances in pm, angles in degrees, rotational constants in MHz, numbers in parentheses are estimated standard deviations. [b] Theoretical results from CCSD(T)/aug-cc-pwCVQZ calculations.[c] Change in bonded distance on moving from the monomer to dimer.

Table 7. Refined r_e Structures and Composition for NaBr Vapor at 920 K Using the EXPRESS Analysis for Vibrational Corrections[a]

		r_e (expt.)	r_e (theory)[b]	Restraint
independent				
p_1	r(Na–Br)$_m$	250.20363(8)	250.8	—
p_2	r(Na–Br)$_d$	267.9(3)	268.2	—
p_3	∠BrNaBr	103.8(3)	104.2	—
p_4	F_d	0.32(2)	—	—
dependent				
d_1	r(Na···Na)	330.6(13)	329.7	—
d_2	r(Br···Br)	421.8(7)	423.2	—
d_3	Δr(Na–Br)[c]	17.7(3)	17.4	—
d_4	B_e ^{23}Na^{79}Br	4534.4661(28)	—	4534.4673(30)

[a] Distances in pm, angles in degrees, rotational constants in MHz, numbers in parenthesis are estimated standard deviations. [b] Theoretical results from CCSD(T)/aug-cc-pwCVQZ calculations. [c] Change in bonded distance on moving from the monomer to dimer.

Table 8. Refined r_e Structures and Composition for NaI Vapor at 848 K Using the EXPRESS Analysis for Vibrational Corrections[a]

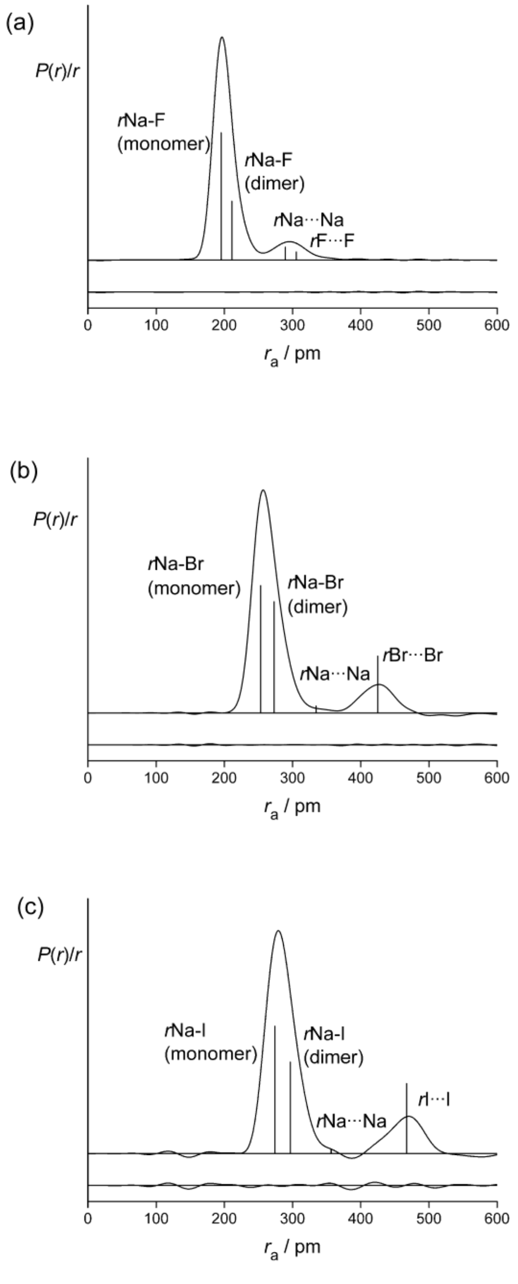
		r_e (expt.)	r_e (theory)[b]	Restraint
Independent				
p_1	$r(\text{Na–I})_m$	271.1454(10)	272.1	—
p_2	$r(\text{Na–I})_d$	291.8(10)	290.7	—
p_3	$\angle$INaI	105.8(9)	107.3	—
p_4	F_d	0.28(2)	—	—
Dependent				
d_1	$r(\text{Na}\cdots\text{Na})$	352.2(42)	344.6	—
d_2	$r(\text{I}\cdots\text{I})$	465.4(20)	468.3	—
d_3	$\Delta r(\text{Na–I})$[c]	20.6(6)	18.6	—
d_4	B_e $^{23}\text{Na}^{127}\text{I}$	3531.7187(27)	—	3531.7187(30)

[a] Distances in pm, angles in degrees, rotational constants in MHz, numbers in parenthesis are estimated standard deviations. [b] Theoretical results from CCSD(T)/aug-cc-pwCVQZ calculations. [c] Change in bonded distance on moving from the monomer to dimer.

The proportion of dimer in the vapor (p_4) was fixed at various values and the refinement process was repeated. The variation in R_G with the proportion of dimer in the vapor was plotted and is shown in Figures S21–S23 for sodium fluoride, sodium bromide, and sodium iodide, respectively. Also shown on each plot is the 95% confidence limit ($\approx 2\sigma$) calculated using the tables of Hamilton.[67] The final proportion of dimer was 0.20(2) for sodium fluoride, 0.32(2) for sodium bromide, and 0.28(2) for sodium iodide. The respective R_G factors for the final refinements were 0.036, 0.033, and 0.114.

The final radial-distribution curves are given in Figure 2, molecular-scattering intensity curves are given in Figures S24–S26 and least-squares correlation matrices are in Tables S10–S12.

Figure 2. Experimental and difference (experimental – theoretical) radial-distribution curves, $P(r)/r$, for (a) sodium fluoride, (b) sodium bromide, and (c) sodium iodide. Before Fourier inversion the data were multiplied by $s\cdot\exp(-0.00002s^2)/(Z_{\mathrm{Na}} - f_{\mathrm{Na}})(Z_{\mathrm{X}} - f_{\mathrm{X}})$, where X = F, Br or I.



The success of the refinements can be gauged by the R_{G} factors together with the experimental minus theoretical difference curves for both the molecular-scattering intensity and radial-distribution curves. All of these factors point towards much more accurately determined structures with respect to previous refinements.[17–19]

Tables 9–11 compare the results of these new refinements with those of previous work,[17–19] those obtained from refinements performed using the best available traditional methods of vibrational correction (which allow for cubic anharmonicity by taking third derivatives of the energy, $r_{a3,1}$) and the highest level theoretical results.

Table 9. Comparison of Results from Different Methods of Analysis for NaF Vapor[a]

parameter	Hartley *et al.*[1,54] (r_a)	SHRINK ($r_{a3,1}$)	EXPRESS (r_e)	theory[b] (r_e)
r(Na–F)$_m$	194.4(1)[c]	192.5942(2)	192.5942(2)	192.9
r(Na–F)$_d$	208.1 (5)[c]	209.4(4)	207.3(4)	206.7
∠(FNaF)	94.7(4)[c,d]	93.3(9)	92.8(6)	93.9
Δr(Na–F)	13.7	16.8(4)	14.7(4)	13.8
F_d	0.31(1)[c,e]	0.19(2)[c]	0.20(1)[c]	—
R_G	0.039	0.038	0.036	—

[a] Distances in pm, angles in degrees. [b] Calculated using CCSD(T)/aug-cc-pwCVQZ (see text for further details). [c] Uncertainties converted to 1σ. [d] Reanalyzed value; see Reference 55. [e] Converted from quoted mole fraction to proportion of NaF units existing as dimer (see Equation 1).

Table 10. Comparison of Results from Different Methods of Analysis for NaBr Vapor[a]

parameter	Hartley *et al.*[1] (r_a)	SHRINK ($r_{a3,1}$)	EXPRESS (r_e)	theory[b] (r_e)
r(Na–Br)$_m$	253.7(6)[c]	250.20364(8)	250.20363(8)	250.8
r(Na–Br)$_d$	274.0(17)[c]	267.6(3)	267.9(3)	268.2
∠(BrNaBr)	101.6(9)[c]	104.2(4)	103.8(3)	104.2
Δr(Na–Br)	20.3	17.4(4)	17.7(3)	17.4
F_d	0.30(3)[c,d]	0.33(2)[c]	0.32(2)[c]	—
R_G	0.134	0.039	0.033	—

[a] Distances in pm, angles in degrees. [b] Calculated using CCSD(T)/aug-cc-pwCVQZ (see text for further details). [c] Uncertainties converted to 1σ. [d] Converted from quoted mole fraction to proportion of NaBr units existing as dimer (see Equation 1).

Table 11. Comparison of Results from Different Methods of Analysis for NaI Vapor[a]

Parameter	Hartley *et al.*[1] (r_a)	SHRINK ($r_{a3,1}$)	EXPRESS (r_e)	theory[b] (r_e)
$r(\text{Na–I})_{\text{monomer}}$	276.9(8)[c]	271.1454(11)	271.1454(10)	272.1
$r(\text{Na–I})_{\text{dimer}}$	299.8(46)[c]	291.6(10)	291.8(10)	290.7
$\angle$(INaI)	102.5(23)[c]	106.1(8)	105.8(8)	107.3
Δr(Na–I)	22.9	20.6(10)	20.6(10)	18.6
F_d	0.20(10)[c,d]	0.28(2)[c]	0.28(2)[c]	—
R_G	0.135	0.115	0.114	—

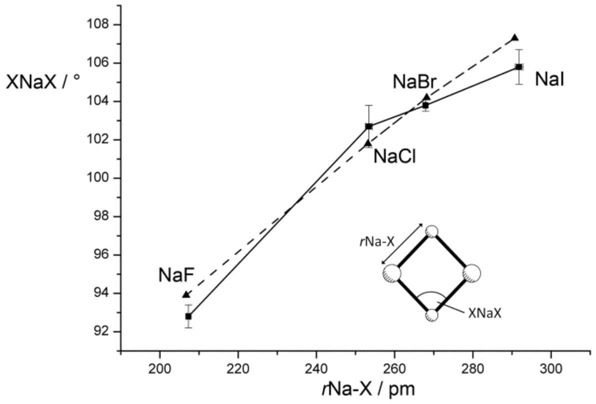
[a] Distances in pm, angles in degrees. [b] Calculated using CCSD(T)/aug-cc-pCVQZ (see text for further details). [c] Uncertainties converted to 1σ. [d] Converted from quoted mole fraction to proportion of NaI units existing as dimer (see Equation 1).

All of the structures obtained using the EXPRESS method show improved estimated standard deviations (ESDs) for the refined parameters when compared with previous results and traditional approaches. When comparing experiment and theory the best comparison is that of the dimer expansion [Δr(Na–X), the difference between the dimer and monomer bond length]. As this is a distance difference we tend to get cancellation of errors for theoretical results. The EXPRESS method brings the dimer expansion to within around two ESDs of the calculated value for sodium fluoride whereas the best traditional approach ($r_{a3,1}$) is over seven ESDs away. For sodium bromide the $r_{a3,1}$ and EXPRESS approaches are within one ESD of the best theoretical value. For sodium iodide the EXPRESS and $r_{a3,1}$ refinements give identical values (20.6 pm) for the dimer expansion. Both reproduce the theoretical result to within two ESDs.

Other notable results include the proportion of dimer present in these vapors. The proportions of dimer for sodium chloride[3] and bromide agree reasonably well with those obtained in previous studies of Mawhorter *et al.*[1] and Hartley *et al.*.[17–19] However, for sodium fluoride the reanalysis of the data shows a decrease in the amount of dimer of around 10%, which is seen both in the $r_{a3,1}$ and EXPRESS (r_e) analyses. For sodium iodide there is an increase of about the same amount, although here the error bars are larger and the second original analysis with more mean amplitudes refining was also consistent with a larger amount. This point illustrates the importance of accurate vibrational corrections when studying systems with such strongly correlated parameters.

Figure 3 shows a graphical representation of the rhombic structural parameters for all the reanalyzed sodium halide dimers, including NaCl.[3] The plot shows a more pronounced curve for the experimental results than for the theoretical calculations. However, this curvature may be reduced somewhat by the inclusion of three-atom scattering into the analysis for sodium iodide, and perhaps for sodium bromide, as was the case for Cs_2Cl_2 and K_2I_2 described in Reference 16.

Figure 3. Comparison of the XNaX angles and Na–X distances for the sodium halide dimer structures. The square data points are experimental values obtained using the GED EXPRESS method, and triangular data points are theoretical values obtained at the CCSD(T)/aug-cc-pCVQZ level. Error bars represent 1σ.



■ CONCLUSIONS

Experimental equilibrium structures have been determined for the sodium halide dimers. This was achieved by employing the recently developed EXPRESS method, which allowed for the calculation of vibrational correction terms that are the most accurate to date. The equilibrium structures were determined for both the monomers and the dimers together with the proportion of vapor existing as dimer. These structures made use of *all* the available information (GED, MW, and *ab initio* calculations). The experimental results are encouraging, giving good agreement with theory, although it is possible that further improvements could be achieved by including multiple-scattering effects for sodium iodide.

■ ASSOCIATED CONTENT

Supporting Information

Experimental parameters for the GED refinements (Table S1); theoretical (harmonic) and experimental vibrational wavenumbers for all three monomers and dimers (Table S2); RMS amplitudes of vibration and distance corrections for NaBr and NaI (Table S3–S6); refined RMS amplitudes of vibration and associated r_a distances for all three refinements (Table S7–S9); least-squares correlation matrices for all three refinements (Table S10–S13); plots of changes in energy with changes in vibrational mode parameter (ρ) for all vibrational modes for all monomer and dimer species (Figures S1–S20); variations of R factor with amount of dimer for all three refinements (Figures S21–S23); molecular scattering intensities and difference curves for all three refinement (Figures S24–26). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ GRAPHICAL ABSTRACT