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# Prediction and experimental comparison of deuterium quadrupole coupling constants in some bifluoride salts: An extreme example of symmetric hydrogen bonding in different crystalline environments

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The electric field gradient (EFG) at the deuterium nucleus of the bifluoride ion, a linear symmetrically H-bonded system, has been calculated using *ab initio* Hartree–Fock SCF, singles and doubles CI, and coupled pair functional methods using basis sets ranging from double zeta to the [7,5,2,1,5,4,2] contracted Gaussian set. For the free  $\text{DF}_2^-$  ion, the EFG and the resulting nuclear quadrupole coupling constant (nqcc) are found to be very low and positive in sign, and to display marked dependences on basis set, and the effects of electron correlation and vibrational averaging. In particular, we note a peculiarly extreme basis-set limit problem for deuterium EFGs in symmetric H-bonded molecules. The effects of the crystal lattice on the nqcc have been calculated for the sodium, potassium, and ammonium bifluorides taking into account: the direct contribution of the lattice to the EFG as modeled by a point-charge distribution; its polarizing effect on an individual  $\text{DF}_2^-$  ion using two different methods; and also the effects of librational averaging. The predicted deuterium nqccs and asymmetry parameters ( $\eta$ ) in the bifluoride salts are compared with the free-ion values ( $\eta$  necessarily zero). While our predicted nqcc in  $\text{KDF}_2$  of  $55 \pm 3$  kHz is consistent with the only reported experimental value of  $58 \pm 10$  kHz [R. Blinc *et al.*, Chem. Phys. Lett. **48**, 596 (1977)], the calculated  $\eta$  value of  $0.07 \pm 0.01$  is at serious variance with the experimental value of  $0.4 \pm 0.1$ . As our treatment of the crystal lattice effects is quite comprehensive this disagreement requires further investigation. We have predicted a significantly higher nqcc for  $\text{NaDF}_2$  of  $83 \pm 3$  kHz, but, again, with a very small  $\eta$  value of  $0.04 \pm 0.01$ .

## I. INTRODUCTION

The electric field gradient (EFG) at a nucleus in a molecule is very sensitive to changes in the electron distribution due, for instance, to chemical substitution, intermolecular association, or solid-state effects. In recent years a considerable amount of information on the effect of H bonding on nuclear quadrupole coupling constants (nqccs), the experimental measure of EFG, in both solids and gas-phase using nqr and microwave spectroscopies has accumulated which we have sought to interpret using theoretical methods.<sup>1–6</sup> Of particular interest were  $^2\text{H}$  nqr results for symmetric H bonds in some carboxylic acid salts; these showed very low nqcc values ( $\sim 40$ – $60$  kHz) with unusually large EFG asymmetry parameter  $\eta$  values ( $\sim 0.3$ – $0.4$ ).<sup>7–11</sup> In our earlier study of the hydrogen biformate anion at the SCF level,<sup>3</sup> we noted problems in computing EFGs for hydrogens involved in symmetric H bonds due to their strong dependence on internuclear separation; this suggested the importance of considering vibrational and basis-set effects in greater detail. So, in order to define more clearly the level of theory necessary for accurate prediction of  $^2\text{H}$  nqccs in solids, we have chosen to study the simplest such species, the bifluoride anion  $\text{HF}_2^-$ . The H bond in  $\text{HF}_2^-$  is also the shortest, with an  $\text{F}\cdots\text{F}$  distance of  $2.30$  Å,<sup>12</sup> and strongest, with a dissociation energy of  $39 \pm 1$  kcal/mol<sup>13</sup> for the gas-phase ion.

Although the structure, vibrational spectroscopy, and H-bond energy of  $\text{HF}_2^-$  have been studied intensively both experimentally and theoretically, and in both solids and gas phase,<sup>14</sup> the literature for EFGs and nqccs is more sparse. From a deuteron NMR study of polycrystalline  $\text{KDF}_2$ , Blinc *et al.*<sup>15</sup> reported a  $^2\text{D}$  nqcc of  $58 \pm 10$  kHz, an  $\eta$  value of  $0.4 \pm 0.1$ , and an F–D distance of  $1.13 \pm 0.03$  Å. Analysis of neutron diffraction data for  $\text{KHF}_2$  indicated a very short linear  $\text{F}\cdots\text{F}$  bond of  $2.277 \pm 0.006$ <sup>16</sup> or  $2.292 \pm 0.004$  Å<sup>17</sup> with corrections for thermal motions, although neither refinement was able to distinguish a linear symmetric F–H–F ion from a linear one in which the hydrogen occupies two equally probable positions on either side of the center. However, the NMR study of Blinc *et al.*<sup>15</sup> and earlier NMR studies for  $\text{KHF}_2$  (H–F distance of  $1.153 \pm 0.005$ ,<sup>18</sup>  $1.138 \pm 0.004$ ,<sup>19</sup> or  $1.14 \pm 0.01$  Å<sup>20</sup> with motional corrections) established that the ion is centered to within  $0.03$ <sup>15</sup> or  $0.025$  Å.<sup>19</sup> Similarly short  $\text{F}\cdots\text{F}$  distances have been found for some other bifluoride salts by solid NMR and diffraction studies<sup>14</sup>; these results are of interest for the present work because of the differing crystal environments of the  $\text{HF}_2^-$  ion. Because the EFG tensor is traceless, the principal component  $eq_{zz}$  is necessarily along the bond direction and the asymmetry parameter  $\eta$  is necessarily zero for an isolated linear  $\text{HF}_2^-$  ion; hence, deviations from zero

in solids, as for  $\text{KDF}_2$ ,<sup>15</sup> must be due to crystal-field induced distortions which would be expected to be symmetry dependent.

At room temperature the  $\text{KHF}_2$ ,  $\text{RbHF}_2$ , and  $\text{CsHF}_2$  salts ( $\alpha$  forms) are isostructural with tetragonal unit cells, but undergo a phase transition to cubic  $\beta$  forms at higher temperatures<sup>21</sup>; the F–H–F structure of the rubidium and caesium salts has been found by solid-state NMR to be similarly symmetric and centered.<sup>20,22</sup> The  $\text{LiHF}_2$  and  $\text{NaHF}_2$  salts both contain rhombohedral/hexagonal unit cells<sup>21,23,24</sup>; a neutron diffraction study<sup>24</sup> of  $\text{NaHF}_2$  and  $\text{NaDF}_2$  found a F–H–F distance of  $2.264 \pm 0.003$  Å and a F–D–F distance of  $2.265 \pm 0.007$  Å, and a solid-state NMR study of  $\text{NaHF}_2$  suggested a centered bond.<sup>22</sup> Thallous bifluoride ( $\text{TlHF}_2$ ) is cubic and possibly isomorphous with the  $\beta$  forms of the  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$  salts<sup>21</sup>; solid-state NMR studies suggest a centered symmetric H bond with a  $\text{F}\cdots\text{F}$  distance of 2.332<sup>22</sup> or  $2.32 \pm 0.02$  Å.<sup>25</sup> Several NMR studies<sup>22,26,27</sup> for some alkali earth mixed bifluoride salts [i.e., containing one or more bifluoride ions, with or without additional fluoride ions] have found examples of both centered symmetric [e.g.,  $\text{Ca}^{2+} \cdot (\text{HF}_2^-)_2$ ] and asymmetric [e.g.,  $\text{Sr}^{2+} \cdot \text{F}^- \cdot (\text{HF}_2^-)$  and  $\text{Ba}^{2+} \cdot \text{F}^- \cdot (\text{HF}_2^-)$ ] H bonds.

For more complex cations: the ammonium salt crystallizes in the orthorhombic space group with  $\text{F}\cdots\text{F}$  distances for the two inequivalent bifluoride ions determined to be  $2.269 \pm 0.005$  and  $2.275 \pm 0.005$  Å in an x-ray study,<sup>28</sup> and  $2.28 \pm 0.01$  Å (motionally corrected) from an NMR study which also suggested a centered symmetric H bond.<sup>29</sup> For the *p*-toluidinium salt, which is also orthorhombic but with the bifluoride ion no longer at a center of symmetry; although a neutron study<sup>30</sup> suggested an asymmetric H bond with  $\text{F}\cdots\text{F}$  distance  $2.260 \pm 0.004$  Å and F–H distances of  $1.025 \pm 0.006$  and  $1.235 \pm 0.006$  Å, x-ray<sup>31</sup> and NMR<sup>29</sup> results are more consistent with a centered structure with distances  $2.276 \pm 0.005$  or  $2.28 \pm 0.01$  Å. However, for another salt, hydrazine hydrofluoride ( $[\text{N}_2\text{H}_6]^{2+} \cdot [\text{HF}_2^-]_2$ ), an NMR study<sup>32</sup> suggested a rhombohedral/hexagonal unit cell and indicated an asymmetric H bond with a  $\text{F}\cdots\text{F}$  distance of  $2.402 \pm 0.002$  Å and F–H distance of  $1.040 \pm 0.005$  Å (without motional corrections), i.e., the hydrogen atom is displaced by  $0.161 \pm 0.005$  Å from the center of the bond. It is apparent from this review that a wealth of structural data is available for simple bifluoride salts displaying varying crystal forms and unit cell parameters, and, hence, varying magnitudes of crystal-field strength and asymmetry.

The IR and Raman vibrational spectra of the bifluoride ion have been studied in a variety of solid salts, salt solutions, and hydrocarbon suspensions,<sup>12,14,33,34</sup> as an ion pair<sup>35</sup> or free ion<sup>36</sup> in solid argon, and, most recently, for the free gas-phase ion.<sup>12</sup> The three fundamental frequencies correspond to symmetric ( $\nu_1$ ) and asymmetric ( $\nu_3$ ) stretches, and a degenerate bending mode ( $\nu_2$ ), with typical values of 600 ( $\nu_1$ ), 1250 ( $\nu_2$ ), and 1450  $\text{cm}^{-1}$  ( $\nu_3$ ) for  $\text{HF}_2^-$ , and 600, 1000, and 1000  $\text{cm}^{-1}$  for  $\text{DF}_2^-$ . In  $\text{KHF}_2$  and  $\text{KDF}_2$ , but not in the sodium salts, the degeneracy of the bending mode is split by 25 and 17  $\text{cm}^{-1}$ , respectively, due to crystal site effects.<sup>33</sup>

Several theoretical and empirical potential surfaces<sup>37–40</sup> have been constructed in order to calculate the vibrational structure; the polynomial fit used by Almlöf<sup>38</sup> for his SCF surface accounting for the linear stretches only was judged adequate for prediction of the lower-lying vibrational states.<sup>41</sup> The study of Lohr and Sloboda<sup>40</sup> produced a polynomial representation of the potential surface corresponding to the bending and asymmetric stretch displacements. For the symmetric stretch, which corresponds to linear displacements of the fluorine atoms about a central hydrogen (i.e., fluctuation in the  $\text{F}\cdots\text{F}$  distance), theory predicts only a small increase of 3–6  $\text{cm}^{-1}$ <sup>38,41,42</sup> in  $\nu_1$  upon deuteration of the free ion; this is consistent with the small negative isotopic shift found for the  $\text{F}\cdots\text{F}$  distance.<sup>24,38,41</sup>

With respect to the asymmetric stretching mode, which corresponds largely to linear displacements of the hydrogen from the central position, the experimental and theoretical literature is quite complex. The mode is characterized by a large negative anharmonicity, high IR and Raman intensities, considerable variation in frequency among phases and crystal forms, and deviations from the Redlich–Teller rule for  $\nu_3(\text{H})/\nu_3(\text{D})$ .<sup>12,14,33,36,42</sup> All these effects are consistent with a shallow protonic well and immense charge redistribution occurring during off-center movements of the hydrogen, as found theoretically.<sup>39,42,43</sup> Doubts about the adequacy of the SCF description for  $\text{HF}_2^-$ , which reportedly places too little charge on the hydrogen atom,<sup>39</sup> have been abundantly confirmed by two recent large-scale theoretical studies,<sup>42,44</sup> which report “unprecedented” variation in  $\nu_3$  values with level of theory (size and type of basis set, and type of correlation treatment).

A previous SCF calculation for  $\text{HF}_2^-$  with a limited basis set<sup>43</sup> found similarly extreme  $r$  dependence, both for the  $\text{F}\cdots\text{F}$  distance and off-center displacements, for the hydrogen EFGs as did our study for the biformate anion,<sup>3</sup> while an early SCF study which investigated the effect of basis set on hydrogen EFGs drew particular attention to the variability for  $\text{HF}_2^-$ .<sup>45</sup> Our earlier work<sup>3</sup> also raised again<sup>45</sup> the question of the sign of the  $^2\text{H}$  nqcc for symmetric H bonds, i.e., whether it might be negative, as this quantity cannot, in general, be determined experimentally. As discussed previously,<sup>3</sup> there are unique problems in predicting hydrogen EFGs (as distinct from those for heavier nuclei) theoretically because of their sensitivity to the electron and nuclear distributions of surrounding atoms; this sensitivity is both extreme and longer range for symmetric H bonds.<sup>3</sup> For this reason it is unlikely that two recent general theoretical treatments which sought to improve the wave function selectively with respect to hydrogen EFGs<sup>46,47</sup> would be useful for symmetrically H-bonded species including  $\text{HF}_2^-$ .

In view of the complexity summarized above it is apparent that accurate theoretical prediction of the complete EFG tensor of hydrogen in the bifluoride ion in solids should represent a considerable challenge. In this paper we have addressed this multifaceted problem by considering the effects on the hydrogen EFG of: basis-set variation and the inclusion of electron correlation; geometry relaxation; vibrational averaging; and crystal-field contributions, both static and induced (Sternheimer shielding<sup>48–50</sup> or crystal–lattice polar-

ization) together with librational corrections, modeled from the known structures of some simple salts. For comparison and discussion of basis-set incompleteness, some EFG results for the hydrogen fluoride molecule are also included.

## II. THEORY AND COMPUTATIONAL METHODS

### A. The quantum chemical calculation of electric field gradients

The interaction between the nuclear quadrupole  $eQ(N)$  and the electric field gradient at a nucleus  $N$  is usually characterized by the nuclear quadrupole coupling constant (nqcc) given as

$$\chi(N) = eQ(N)eq(N)/h = e^2qQ/h \quad (1)$$

and the asymmetry parameter  $\eta$ , defined as

$$\eta = (V_{XX} - V_{YY})/V_{ZZ}. \quad (2)$$

In Eq. (1)  $e$  is the proton charge,  $h$  is Planck's constant, and  $eq(N) \equiv V_{ZZ}(N)$  is the largest principal component of the EFG tensor. The principal axes are labeled according to the convention  $|V_{ZZ}| > |V_{YY}| > |V_{XX}|$ . A given component of the Cartesian EFG tensor at a fixed molecular geometry is generally evaluated as the expectation value (EV) of the corresponding operator, i.e., as the sum of nuclear and electronic terms:

$$V_{\alpha\beta}(N) = e \left\{ \sum_{I \neq N} Z_I (3R_{\alpha IN} R_{\beta IN} - \delta_{\alpha\beta} R_{IN}^2) / R_{IN}^5 - \langle \Psi | (3r_{\alpha N} r_{\beta N} - \delta_{\alpha\beta} r_N^2) / r_N^5 | \Psi \rangle \right\}, \quad (3)$$

where  $\{R_\alpha\}$  and  $\{r_\alpha\}$  represent the nuclear and electron Cartesian coordinates, respectively,  $R_{IN}$  is the distance between nucleus  $I$  (with charge  $eZ_I$ ) and nucleus  $N$ , and  $\Psi$  is the electronic wave function of the molecule.

As discussed elsewhere in detail,<sup>51,52</sup> the electronic contribution  $V_{\alpha\beta}(N)_{el}$  to a given component of the EFG tensor can also be written as an energy derivative (ED),

$$V_{\alpha\beta}(N)_{el} = \frac{\partial E(Q)}{\partial Q_{\alpha\beta}} \bigg|_{Q=0}, \quad (4)$$

where  $Q$  represents an effective nuclear quadrupole tensor with components  $Q_{\alpha\beta}$ , since the Hamiltonian (in atomic units) for a molecule with  $Q$  can be written as

$$\hat{H}(Q) = \hat{H}(0) + \sum_{\alpha,\beta} Q_{\alpha\beta} \hat{V}_{\alpha\beta}, \quad (5)$$

where  $\hat{H}(0)$  is the unperturbed Hamiltonian. The derivative in Eq. (4) can be written explicitly as

$$\frac{\partial E(Q)}{\partial Q_{\alpha\beta}} \bigg|_{Q=0} = \langle \Psi(0) | \hat{V}_{\alpha\beta} | \Psi(0) \rangle + 2 \left\langle \frac{\partial \Psi(Q)}{\partial Q_{\alpha\beta}} \bigg|_{Q=0} \right| \hat{H}(0) | \Psi(0) \rangle, \quad (6)$$

where  $\Psi(0)$  is the unperturbed electronic wave function,  $\hat{V}_{\alpha\beta}$  represents an electronic component of the EFG operator and it has been assumed that  $\hat{H}(0)$  is Hermitian. If  $\Psi(0)$  is an exact or fully optimized wave function, the Hellmann–Feynman theorem is satisfied, i.e., the second term in Eq. (6) vanishes and the EV and ED formalisms are equivalent.<sup>54–59</sup> Thus, SCF and MCSCF wave functions satisfy the Hellmann–Feynman theorem in the case of first-order properties while limited configuration-interaction-type wave functions expanded in terms of SCF molecular orbitals do not. It has been strongly argued that the ED method is the formally correct approach to the calculation of properties when the Hellmann–Feynman theorem is not satisfied<sup>54–58</sup> and the results that have accumulated during the last few years provide strong support for the notion that the ED formalism yields the more accurate property values.<sup>51–62</sup> As shown elsewhere,<sup>59</sup> this is because the ED method accounts for the first-order effects of the orbital relaxation in a limited CI wave function, i.e., the variational flexibility of the wave function is exploited to a larger degree in the ED formalism than is implicit in the EV approach. Consequently, where the greatest accuracy is sought the ED method will be used in this work to calculate the EFG tensor.

The electronic wave functions used in this work were generated by three methods: Hartree–Fock SCF, configuration interaction with all single and double excitations from the SCF reference (CI-SD), and the coupled-pair functional (CPF) methods. The CPF formalism<sup>63–65</sup> is closely related to the CEPAL scheme of Meyer<sup>66</sup> and Ahlrichs.<sup>67,68</sup> In the CI-SD and CPF calculations the fluorine 1s orbitals are frozen to excitations.

A number of basis sets have been used in an effort to determine systematically the basis-set requirements for the

TABLE I. Basis sets used in the FHF<sup>−</sup> calculations.

Contracted basis	Parent basis (primitive or contracted)	Details of additional (polarization and diffuse) functions
[5,3;2] <sup>a</sup>	(9,5;4)	
[5,3,1;2,1]	[5,3;2]	3d <sub>F</sub> ( $\zeta = 1.0$ ), 2p <sub>H</sub> ( $\zeta = 1.0$ )
[6,4;4] <sup>b</sup>	(11,7;6)	
[6,4,1;4,1]	[6,4;4]	3d <sub>F</sub> ( $\zeta = 1.0$ ), 2p <sub>H</sub> ( $\zeta = 1.0$ )
[6,4,2;4,2]	[6,4;4]	3d <sub>F</sub> ( $\zeta = 1.6, 0.5$ ), 2p <sub>H</sub> ( $\zeta = 1.0, 0.3$ )
[7,5,2;5,3]	[6,4,2;4,2]	1s <sub>F</sub> ( $\zeta = 0.08$ ), 2p <sub>F</sub> ( $\zeta = 0.05$ ), 1s <sub>H</sub> ( $\zeta = 0.02$ ), 2p <sub>H</sub> ( $\zeta = 0.05$ )
[6,4,2,1;4,2,1]	[6,4,2;4,2]	4f <sub>F</sub> ( $\zeta = 1.0$ ), 3d <sub>H</sub> ( $\zeta = 0.6$ )
[7,5,2,1;5,3,1]	[7,5,2;5,2]	4f <sub>F</sub> ( $\zeta = 1.0$ ), 3d <sub>H</sub> ( $\zeta = 0.6$ )
[6,4,2,1;4,3,2]	[6,4,2,1;4,2,1]	2p <sub>H</sub> ( $\zeta = 3.0$ ), 3d <sub>H</sub> ( $\zeta = 2.0$ )
[7,5,2,1;5,4,2]	[7,5,2,1;5,3,1]	2p <sub>H</sub> ( $\zeta = 3.0$ ), 3d <sub>H</sub> ( $\zeta = 2.0$ )

<sup>a</sup> Contraction: 5,1,1,1,1/3,1,1/3,1.

<sup>b</sup> Contraction: 6,1,1,1,1,1/4,1,1,1/3,1,1,1.

accurate prediction of the EFG tensor at the  $^2\text{H}$  nucleus in  $\text{HF}_2^-$ . The standard parent basis is Huzinaga's (11,7;6) primitive Gaussian set<sup>69</sup> contracted to [6,4;4]. This basis was then systematically extended by polarization functions as well as by diffuse 1s and 2p orbitals on both fluorine and hydrogen atoms. The largest basis used in this work is a [7,5,2,1;5,4,2] contracted Gaussian set. For comparison two smaller basis sets were also used, the [5,3;2] set that derives from Huzinaga's (9,5;4) primitive set<sup>69</sup> and the [5,3,1;2,1] basis which includes a single set of polarization functions. A summary of the basis sets is given in Table I.

The electronic calculations reported in this work were performed using the CYBER 205 version of the COLUMBUS programs<sup>63,64,70</sup> on the CYBER 205 of CSIRO Australia.

## B. Vibrational averaging

As the available experimental evidence suggests that the  $^2\text{H}$  nqcc for  $\text{HF}_2^-$  is very small,<sup>15</sup> it is especially important to consider the effects of zero-point vibrations in this molecular system. The vibrational wave functions for the linear symmetric  $\text{HF}_2^-$  ion were generated by solving the appropriate Schrödinger equation(s) variationally using products of harmonic-oscillator eigenstates as basis functions and assuming no coupling between the linear stretches and the degenerate bending modes. This approximation appears to be well justified, since the extensive theoretical study of Janssen *et al.*<sup>42</sup> has demonstrated that the amount of anharmonicity in the bending mode is very small. The function for the potential energy surface is then written as a polynomial:

$$E = E_e + \sum_{i,j} a_{ij} (R - R_e)^i r^j + \sum_i b_i y^i, \quad (7)$$

where  $R$  is the F...F distance,  $r$  represents the antisymmetric distortion defined as the movement of the H atom away from its equilibrium position, hence it is half the difference of the F-H distances, i.e.,

$$r = (r_{\text{F}_1\text{H}} - r_{\text{F}_2\text{H}})/2, \quad (8)$$

$y$  is the displacement of the H atom perpendicular to the F-H-F molecular axis and  $E_e$  is the equilibrium energy. The principal component of the EFG tensor  $V_{zz}$ , which is along the inertial (molecular) axis for the free ion, is also expanded in the same parameters, viz.

$$V_{zz} = V_{zz}^e + \sum_{i,j} \alpha_{ij} (R - R_e)^i r^j + \sum_i \beta_i y^i, \quad (9)$$

hence, given the (normalized) ground-state vibrational wave function  $|0\rangle$ , the vibrational average of  $V_{zz}$  is simply calculated according to

$$\begin{aligned} \langle V_{zz} \rangle &= V_{zz}^e + \sum_{i,j} \alpha_{ij} \langle 0 | (R - R_e)^i r^j | 0 \rangle \\ &\quad + 2 \sum_i \beta_i \langle 0 | y^i | 0 \rangle, \end{aligned} \quad (10)$$

where the factor of 2 multiplying the second sum is to account for the degeneracy of the bending mode.

## C. Crystal field effects

To estimate the  $^2\text{H}$  nqcc of  $\text{HF}_2^-$  in a crystalline environment, e.g., in sodium, potassium, and ammonium bifluor-

ides, one must account for two major effects: the (static) polarization effect of the crystal lattice on the EFG and the (dynamical) effect of lattice vibrations, i.e., librations.

The approach adopted in this work for the static effects follows that used previously, e.g., in the calculation of solid-state shifts to nqccs in water and ammonia.<sup>6,71,72</sup> Thus, in the presence of a crystal field there will be two types of perturbation to the EFG of the isolated molecule: a direct contribution from the rest of the lattice, as well as an induced term which arises from the response of the molecular wave function to the crystal field. The approach assumes that the electrostatic model is an adequate description of the interionic interactions as, clearly, no account is taken of exchange and charge transfer. To account for the latter phenomena rigorously it would be necessary to perform a quantum mechanical calculation for a "supermolecule" composed of a sufficiently large cluster of ions. However, the size of such a system would almost certainly preclude the use of sufficiently extensive basis sets to accurately resolve the changes in the hydrogen EFG that occur when a  $\text{HF}_2^-$  ion is placed in a crystalline environment. As the interionic distances in the alkali metal and ammonium bifluoride salts are fairly large, we can expect an electrostatic treatment to yield reasonable estimates of the solid-state effects on the hydrogen EFG.

### 1. Point-charge model

The bifluoride ions are modeled by a distribution of point charges, one on each nucleus, chosen so that both the calculated quadrupole moment of  $\text{HF}_2^-$  and the net charge of  $-1e$  are reproduced. The alkali metal ions are represented by point charges of  $+1e$ , while the  $\text{NH}_4^+$  ion is modeled by five charges, one on each atom, chosen on the basis of x-ray data.<sup>28</sup> Full details of the charges are given in the next section. We note at this point, however, that test calculations suggest that the direct contribution of the crystal lattice to the hydrogen EFG is surprisingly insensitive to the finer details of the point-charge distributions, provided that the correct value for the net charge on each species is maintained. Because of the simplicity of the charge distribution model it is easy to include very large numbers of ions in the calculations, in this work typically  $\sim 20\,000$ .

### 2. Sternheimer shielding

The polarizing effect of the lattice on a bifluoride ion and the resulting change in the hydrogen EFG was calculated by perturbation theory, as first proposed by Sternheimer.<sup>48,50,73</sup> Thus, given the external field and field gradient with components  $\epsilon_\alpha$  and  $V_{\alpha\beta}^{\text{ext}}$ , respectively, we write the total EFG at a given nucleus as

$$V_{\alpha\beta} = V_{\alpha\beta}^0 + \sum_\gamma \gamma_{\alpha\beta,\gamma} \epsilon_\gamma + \sum_{\gamma,\delta} (1 + \gamma_{\alpha\beta,\gamma\delta}) V_{\gamma\delta}^{\text{ext}}, \quad (11)$$

where  $V_{\alpha\beta}^0$  are the components of the unperturbed (molecular) EFG and  $\gamma_{\alpha\beta,\gamma}$  and  $\gamma_{\alpha\beta,\gamma\delta}$  are the components of the Sternheimer (anti)shielding tensor which specify the response of the molecule to the external field and field gradient. The shielding tensors, at any level of theory, are readily calculated by the finite-field method. Noting that

$$\gamma_{\alpha\beta,\gamma} = \frac{\partial^2 E}{\partial Q_{\alpha\beta} \partial \epsilon_\gamma} \bigg|_{Q=0, \epsilon=0}, \quad (12)$$

where  $Q_{\alpha\beta}$  are components of the effective nuclear quadrupole moment and

$$\gamma_{\alpha\beta,\gamma\delta} = \frac{\partial^2 E}{\partial Q_{\alpha\beta} \partial V_{\gamma\delta}^{\text{ext}}} \bigg|_{Q=0, V^{\text{ext}}=0} \quad (13)$$

we can obtain the shielding tensors by straightforward numerical differentiation of the total energy of a molecule calculated with a Hamiltonian containing terms for both a finite external field (or field gradient) and a perturbing nuclear quadrupole. If the wave function obeys the Hellmann–Feynman theorem the shielding tensors can be calculated in two different ways, each of which requires only first derivatives to be calculated numerically. In the first scheme we write

$$\gamma_{\alpha\beta,\gamma} = \partial \langle \Psi(\epsilon) | \hat{V}_{\alpha\beta} | \Psi(\epsilon) \rangle / \partial \epsilon_\gamma \big|_{\epsilon=0} \quad (14)$$

and

$$\gamma_{\alpha\beta,\gamma\delta} = \partial \langle \Psi(V^{\text{ext}}) | \hat{V}_{\alpha\beta} | \Psi(V^{\text{ext}}) \rangle / \partial V_{\gamma\delta} \big|_{V^{\text{ext}}=0}, \quad (15)$$

where the normalized wave functions  $\Psi(\epsilon)$  and  $\Psi(V^{\text{ext}})$  have been calculated in the presence of just one perturbation,  $\epsilon$  or  $V^{\text{ext}}$ , i.e., the shielding tensors are calculated by (numerically) differentiating the expectation values of the EFG operator that had been calculated in the presence of the perturbing external field or field gradient. Alternatively, using the second approach, we write

$$\gamma_{\alpha\beta,\gamma} = \partial \langle \Psi(Q) | \hat{\mu}_\gamma | \Psi(Q) \rangle / \partial Q_{\alpha\beta} \big|_{Q=0} \quad (16)$$

and

$$\gamma_{\alpha\beta,\gamma\delta} = (1/3) \partial \langle \psi(Q) | \hat{\theta}_{\gamma\delta} | \psi(Q) \rangle / \partial Q_{\alpha\beta} \big|_{Q=0}, \quad (17)$$

where  $\hat{\mu}$  and  $\hat{\theta}$  are the electric dipole and quadrupole moment operators. The factor of 1/3 arises from the standard definition of the molecular quadrupole moment, viz.,

$$\theta_{\alpha\beta} = \frac{3 \partial E(V^{\text{ext}})}{\partial V_{\alpha\beta}^{\text{ext}}} \bigg|_{V^{\text{ext}}=0}. \quad (18)$$

The second method is generally the more convenient one to use since it involves the use of only one finite perturbing term, the effective nuclear quadrupole moment  $Q$ ; consequently, it is the approach we employed in this work.

### 3. Finite-field (point-charge) SCF

For potassium bifluoride the polarizing effect of the lattice was also calculated by a more direct approach, viz., by including the point charges representing a substantial portion of the crystal in the Hamiltonian of the reference ion. Such a calculation enables us to check the validity of the underlying assumption of the Sternheimer approach, i.e., that the effect of polarizing the bifluoride ions is adequately described by second-order perturbation theory. According to our previous experience<sup>3,4</sup> in calculating the field gradients at deuterium sites, the dominant contribution to the EFG is actually due to the nuclei and electrons of the heavy atoms in the molecule rather than to the hydrogenic electrons. Consequently, the polarization of the fluorine electrons, which is not considered in the Sternheimer-type treatment, may be expected to have a significant effect on the

EFG at the deuterium nucleus. Full details of this calculation will be given in the next section together with the results.

### 4. Librational averaging

In order to calculate the dynamical effect of librational motions on the deuterium nqcc and asymmetry parameter in the various bifluoride crystals we need to calculate the (librational) average of the EFG tensor defined with respect to the appropriate inertial axis. If we allow a given bifluoride ion to rotate away from its equilibrium configuration, i.e., the inertial ( $z$ ) axis, in the  $xz$  and  $yz$  planes by the (small) angles  $\theta_y$  and  $\theta_x$ , respectively, the resulting averaged components of the EFG tensor in the molecular axis system are given by

$$\langle V_{xx} \rangle = V_{xx}^0 \langle \cos^2 \theta_y \rangle + V_{zz}^0 \langle \sin^2 \theta_y \rangle, \quad (19)$$

$$\langle V_{yy} \rangle = V_{yy}^0 \langle \cos^2 \theta_x \rangle + V_{zz}^0 \langle \sin^2 \theta_x \rangle, \quad (20)$$

$$\begin{aligned} \langle V_{zz} \rangle &= V_{xx}^0 \langle \sin^2 \theta_y \rangle + V_{yy}^0 \langle \sin^2 \theta_x \rangle \\ &\quad + V_{zz}^0 (1 - \langle \sin^2 \theta_x \rangle - \langle \sin^2 \theta_y \rangle), \end{aligned} \quad (21)$$

where  $V_{xx}^0$ ,  $V_{yy}^0$  and  $V_{zz}^0$  are the components of the total (static) EFG tensor at the equilibrium configuration. Equations (19)–(21) follow from the transformation properties of the EFG tensor, neglecting higher than quadratic terms in  $\sin \theta_x$  and  $\sin \theta_y$ . The Dirac brackets denote averages over the two librational modes considered. Note that the averaged EFG tensor is traceless as it must be. Given that for a linear molecule, such as the bifluoride ion, the molecular and principal-axis systems coincide, the asymmetry parameter is simply given as

$$\eta = |\langle V_{xx} \rangle - \langle V_{yy} \rangle| / \langle V_{zz} \rangle. \quad (22)$$

For simplicity let us assume that the EFG tensor at the equilibrium configuration is symmetric in the  $xx$  and  $yy$  components, i.e.,

$$V_{xx}^0 = V_{yy}^0 = -(1/2) V_{zz}^0, \quad (23)$$

in which case we obtain the following simple expressions for the principal component of the EFG tensor and the asymmetry parameter:

$$\begin{aligned} \langle V_{zz} \rangle &= V_{zz}^0 [(3/2) \langle \cos^2 \theta_x \rangle \\ &\quad + (3/2) \langle \cos^2 \theta_y \rangle - 2], \end{aligned} \quad (24)$$

$$\begin{aligned} \eta &= |\langle \cos^2 \theta_x \rangle - \langle \cos^2 \theta_y \rangle| / (\langle \cos^2 \theta_x \rangle \\ &\quad + \langle \cos^2 \theta_y \rangle - 4/3). \end{aligned} \quad (25)$$

If we make the further approximation

$$\cos^2 \theta \approx 1 - \theta^2, \quad (26)$$

we obtain

$$\langle V_{zz} \rangle = V_{zz}^0 [1 - (3/2) \langle \theta_x^2 \rangle - (3/2) \langle \theta_y^2 \rangle] \quad (27)$$

and

$$\eta = |\langle \theta_x^2 \rangle - \langle \theta_y^2 \rangle| / (2/3 - \langle \theta_x^2 \rangle - \langle \theta_y^2 \rangle). \quad (28)$$

Thus, the effect of the librations is both to reduce the magnitude of the EFG and, provided the mean-square amplitudes of the librational modes are different, to produce a degree of asymmetry in the EFG tensor. It is obvious from Eq. (28), however, that the mean-square amplitudes of the librational

TABLE II. The total energy ( $E$ ), electric field gradients ( $V_{zz}$ ), and the quadrupole moment ( $\theta$ ) (at center of mass) of  $\text{HF}_2^-$  calculated at the SCF and CI-SD levels of theory at the  $\text{F}\cdots\text{F}$  separation of 2.265 Å using the basis sets of Table I. (All quantities given in atomic units.)

Basis	SCF				CI-SD(EV)				
	$E$	$V_{zz}(\text{H})$	$V_{zz}(\text{F})$	$\theta$	$E_{\text{corr}}^a$	$V_{zz}(\text{H})$	$\Delta V_{zz}(\text{H})^b$	$V_{zz}(\text{F})$	$\theta$
[5,3,2]	-199.524 301	0.151 01	1.2510	-7.4403	-0.280 066	0.185 22	0.034 21	1.2005	-7.3277
[5,3,1;2,1]	-199.544 020	0.052 71	1.1166	-6.6990	-0.407 113	0.086 45	0.033 74	1.0860	-6.5937
[6,4,4]	-199.565 174	0.146 17	1.1521	-7.4951	-0.292 947	0.184 77	0.038 60	1.0924	-7.3915
[6,4,1;4,1]	-199.584 404	0.050 32	1.0482	-6.9028	-0.418 573	0.086 09	0.035 77	1.0127	-6.8109
[6,4,2;4,2]	-199.585 362	0.059 09	1.0402	-6.6667	-0.463 479	0.094 68	0.035 59	0.9982	-6.5568
[7,5,2;5,3]	-199.587 826	0.060 77	1.0354	-6.6992	-0.464 852	0.096 94	0.036 17	0.9932	-6.5906
[6,4,2,1;4,2,1]	-199.586 604	0.041 12	1.0119	-6.7267	-0.497 270	0.074 95	0.033 84	0.9716	-6.5995
[7,5,2,1;5,3,1]	-199.589 006	0.042 65	1.0080	-6.7581	-0.498 512	0.077 04	0.034 40	0.9677	-6.6311
[6,4,2,1;4,3,2]	-199.587 027	0.018 94	1.0133	-6.7171	-0.497 946	0.051 91	0.032 97	0.9746	-6.5874
[7,5,2,1;5,4,2]	-199.589 447	0.020 40	1.0090	-6.7496	-0.499 186	0.053 87	0.033 48	0.9702	-6.6201

<sup>a</sup> Valence correlation energy.<sup>b</sup> Difference between CI-SD and SCF  $V_{zz}(\text{H})$  values.

modes need to be large and very different for a substantial degree of asymmetry to be observed.

### III. RESULTS AND DISCUSSION

#### A. Basis set effects

In agreement with other theoretical studies<sup>38,39,42,44</sup> our preliminary test calculations have shown  $\text{HF}_2^-$  to be linear symmetric, i.e., of  $D_{\infty h}$  symmetry at both the SCF and correlated levels of theory; these calculations used basis sets ranging from double-zeta to triple-zeta plus two polarization functions. Consequently, in our study of basis-set and correlation effects on the  $^2\text{H}$  nqcc the geometry of  $\text{HF}_2^-$  was kept linear symmetric and the  $\text{F}\cdots\text{F}$  bond length was fixed at its experimental value in  $\text{NaDF}_2$ , viz., 2.265 Å.<sup>24</sup> In addition to calculating the total energy and the EFG at the hydrogen nucleus we also computed the quadrupole moment (at the center of mass) and the EFG at the fluorine nucleus. The results for the various basis sets (Table I) are summarized in Table II. The hydrogen EFGs show a very large degree of variation with the basis used, with the SCF values changing by nearly an order of magnitude as the basis is extended. The inclusion of polarization functions is clearly of paramount importance not only for the hydrogen EFG but for all the properties. The diffuse  $s$  and  $p$  orbitals, while having a noticeable effect on the energy and the quadrupole moment, seem to be relatively unimportant for the EFG on hydrogen. We note also the important contribution of the  $3d_{\text{H}}$  orbitals to the hydrogen EFG. This can be attributed to the coupling of  $s$ -type orbitals with  $d$  orbitals by the EFG operator. Hence, even though the hydrogen  $3d$  orbitals contribute little to the wave function and the energy, their contribution to a property such as the EFG can be quite substantial. Similar observations were made by Davidson and Feller<sup>74</sup> in their

study of the molecular properties of water. Although the absolute changes in the fluorine EFG with variation in the basis set are similar to those observed for hydrogen, the larger magnitude of the fluorine EFG means that the relative changes with basis-set variation are quite small. Similar considerations apply to the quadrupole moment: an absolute variation with basis set of  $\sim 1$  a.u. translates to about a 15% relative variation. Further discussion of basis-set incompleteness is deferred to a later section.

#### B. Correlation corrections

In contrast to the changes in the correlation energy as the basis is varied, the correlation corrections to the properties, as calculated by the CI-SD method using the EV formalism, are quite constant. Thus, the hydrogen EFG is increased by  $\sim 0.034$  a.u. as a result of correlation, the correction being larger in absolute value than the best SCF estimate of the EFG. Similarly, electron correlation lowers the fluorine EFG by  $\sim 0.04$  a.u., but increases the quadrupole moment by  $\sim 0.12$  a.u.

In order to assess the contribution of higher-order excitations to the hydrogen EFG we carried out several CPF calculations, using three of the larger basis sets from Table I. As these represent our ultimate attempt to obtain an accurate EFG, the ED formalism [Eq. (4)] has been used. Thus, finite-field calculations were carried out using a Hamiltonian perturbed by an effective nuclear quadrupole of  $\pm 0.001$  a.u., a value small enough to ensure that the derivative  $\partial E / \partial Q|_{Q=0}$  would have negligible contamination from the cubic terms, but large enough to ensure numerical accuracy in calculating the energy differences. The results of the CPF calculations are given in Table III. The CI-SD predictions of the hydrogen EFG from Table II are included for

TABLE III. The hydrogen electric field gradient in  $\text{HF}_2^-$  (in a.u.) calculated at the CI-SD and CPF levels of theory at the  $\text{F}\cdots\text{F}$  separation of 2.265 Å.

Basis	$V_{zz}(\text{H})$			$E_{\text{corr}}(\text{CPF})^a$
	CI-SD(EV)	CI-SD(ED)	CPF(ED)	
[6,4,2,1;4,2,1]	0.074 95	0.074 55	0.087 14	-0.540 022
[7,5,2,1;5,3,1]	0.077 04	0.076 80	0.090 32	-0.542 316
[7,5,2,1;5,4,2]	0.053 87	0.053 60	0.067 07	-0.543 050

<sup>a</sup> Valence correlation energy.



comparison. We note that at the CI-SD level the agreement between the EFGs calculated by the EV and ED formalisms is very good, i.e., the contribution of the non-Hellmann-Feynman term to the EFG is quite small. However, the CPF results are significantly higher than their CI-SD counterparts; hence for the quantitative prediction of the hydrogen EFG the contribution of quadruple and possibly higher-order excitations must be considered.

### C. Variation of hydrogen EFG with F...F distance

Using the [7,5,2,1;5,3,1] basis the energy of  $\text{HF}_2^-$  was calculated at the SCF, CI-SD, and CPF levels of theory at four geometries displaced from  $R = 2.265 \text{ \AA}$  by  $\Delta R \pm 0.05 a_0$  and  $\Delta R \pm 0.10 a_0$ . The equilibrium F...F separation was then determined from the appropriate quartic fits to the energies. We obtained  $R_e(\text{SCF}) = 2.247 \text{ \AA}$ ,  $R_e(\text{CI-SD}) = 2.267 \text{ \AA}$ , and  $R_e(\text{CPF}) = 2.283 \text{ \AA}$ . Thus, our best estimate for the equilibrium F...F distance in free  $\text{HF}_2^-$ , i.e., the CPF value, is slightly larger than both the experimental value for  $\text{NaDF}_2$  and the best theoretical value (CI-SD with Davidson's correction) of Janssen *et al.*,<sup>42</sup>  $2.266 \text{ \AA}$ , who used a basis of comparable size.

The  $R$  dependence of the hydrogen EFG, calculated at the CI-SD level using the EV formalism, is given by the quartic polynomial (in a.u.)

$$V_{zz} = V_{zz}^e - 0.4128(R - R_e) + 0.3657(R - R_e)^2 - 0.2008(R - R_e)^3 + 0.0667(R - R_e)^4 \\ + 1.7556r^2 + 1.7534r^4 - 3.054(R - R_e)r^2 + 1.280(R - R_e)^2r^2 \\ - 0.2450y^2 + 0.1480y^4,$$

where  $R_e$  is the CPF equilibrium distance, viz.,  $4.314 a_0$ . The agreement between the coefficients of  $(R - R_e)^n$  given in Eqs. (29) and (30) is certainly close enough to justify use of the smaller basis to generate the EFG surface. The vibrational wave functions, as discussed in Sec. II, were calculated assuming no coupling between the stretches and the bend; consequently, no cross terms between  $y$  and  $(R - R_e)$  or  $r$  had to be calculated. The potential-energy surface for the stretches was taken from the work of Janssen *et al.*,<sup>42</sup> it had been calculated using the CI-SD method in a triple-zeta basis plus two sets of polarization functions and a set of Rydberg functions (TZ2P + R). The bending potential on the other hand was calculated by the CPF method using the [6,4,2;4,2] basis, utilizing the same grid points as in the EFG calculation. The resulting normal bending-mode frequencies  $\omega_2(\pi_u)$  for  $\text{HF}_2^-$  and  $\text{DF}_2^-$  are  $1349$  and  $967 \text{ cm}^{-1}$ , respectively, in good agreement with the best theoretical estimates of Janssen *et al.*,<sup>42</sup> viz.,  $1360$  and  $974 \text{ cm}^{-1}$ . The corresponding CPF anharmonic frequencies  $\nu_2(\pi_u)$  are  $1384$  and  $985 \text{ cm}^{-1}$ , to be compared with the experimental (solid argon matrix) values of  $1377$  and  $966 \text{ cm}^{-1}$  of McDonald and Andrews<sup>36</sup> and the theoretical values of  $1363$  and  $974 \text{ cm}^{-1}$  of Janssen *et al.*<sup>42</sup> Given the ground-state vibrational wave function for  $\text{DF}_2^-$ , the vibrationally averaged deuterium EFG was calculated according to Eq. (10), using the EFG surface given in Eq. (30). The total vibrational correction to the deuterium EFG has been computed to be  $0.0202 \text{ a.u.}$ , of

$$V_{zz} = 0.06334 - 0.3922(R - R_e) \\ + 0.3599(R - R_e)^2 - 0.2129(R - R_e)^3 \\ + 0.0720(R - R_e)^4, \quad (29)$$

where  $R_e$  is the CPF equilibrium separation, viz.,  $4.314 a_0$ . From this equation it is possible to predict the change in the EFG which accompanies the small increase in  $R_e$  (from  $2.265$  to  $2.283 \text{ \AA}$ ) as  $-0.0137 \text{ a.u.}$  (or  $-9.2 \text{ kHz}$  in the nqcc). When this correction is applied to our most accurate CPF result from Table II, we obtain a hydrogen EFG value of  $0.0534 \text{ a.u.}$  As we have found the  $R$  dependence of the EFG to be fairly independent of the level of theory or basis set used, the above procedure for calculating the effect of geometry changes is well justified.

### D. Vibrational averaging

In order to calculate the ground-state vibrational average of the deuterium EFG in  $\text{DF}_2^-$  the field gradient was calculated at a number of distorted geometries [ $\pm 0.05 a_0$ ,  $\pm 0.10 a_0$  for  $(R - R_e)$ ,  $r$  and  $y$ ] at the CI-SD(EV) level of theory using the [6,4,2;4,2] basis. The calculated points were then fitted to the polynomial of Eq. (9) resulting in the expression (in a.u.)

(30)

which  $0.0351 \text{ a.u.}$  is due to the stretches and  $-0.0149 \text{ a.u.}$  is due to the degenerate bending mode. The largest single contribution to the vibrational correction is the harmonic antisymmetric-stretch term ( $0.0496 \text{ a.u.}$ ); this is a direct consequence of the strong dependence of the EFG on  $r$ , as seen in Eq. (32). Consequently, the vibrationally averaged EFG at the  $^2\text{H}$  nucleus in free  $\text{DF}_2^-$  is estimated to be  $0.0736 \text{ a.u.}$  which corresponds to a nqcc of  $49.5 \text{ kHz}$ ; we have used a conversion factor of  $672 \text{ kHz/a.u.}$  which is based on a figure of  $0.286 \text{ fm}^2$  for the deuterium quadrupole.<sup>75-77</sup>

As the root-mean-square vibrational amplitudes associated with the movement of the deuterium atom are fairly large, viz.,  $\sim 0.18 a_0$ , it may seem that the distortions (up to  $\pm 0.10 a_0$ ) are too small to describe the  $r$  and  $y$  dependences of the EFG surface accurately. However, check calculations at the SCF level using displacements up to  $0.2 a_0$  indicate that Eq. (30) gives the vibrational correction to the deuterium EFG to within 1% of the quoted value; the EFG surface calculated at the SCF level closely resembles the correlated surface [Eq. (30)].

### E. Solid state effects

The only experimental estimate of the  $^2\text{H}$  EFG in the bifluoride ion is that of Blinc *et al.*<sup>15</sup> from NMR measurements on polycrystalline  $\text{KDF}_2$ ; they reported a nqcc of  $58 \pm 10 \text{ kHz}$  and an anisotropy value  $\eta$  of  $0.4 \pm 0.1$ . While



TABLE IV. Calculated external electric field gradients ( $V_{\alpha\beta}^{\text{ext}}$ ) (in a.u.) at the deuterium nucleus in crystalline sodium, potassium, and ammonium bifluorides.<sup>a,b</sup>

Crystal	$V_{xx}^{\text{ext}}$	$V_{yy}^{\text{ext}}$	$V_{zz}^{\text{ext}}$	$V_{xy}^{\text{ext}}$	$V_{xz}^{\text{ext}}$	$V_{yz}^{\text{ext}}$
NaDF <sub>2</sub>	-0.0196	-0.0221	0.0418	-0.0021	0.0	0.0
KDF <sub>2</sub>	-0.0027	-0.0081	0.0108	0.0	0.0	0.0
NH <sub>4</sub> DF <sub>2</sub> (1)	0.0031	-0.0043	0.0012	0.0020	-0.0008	-0.0004
NH <sub>4</sub> DF <sub>2</sub> (2)	0.0023	-0.0035	0.0011	0.0010	0.0	0.0022

<sup>a</sup>z axis is the molecular axis.<sup>b</sup>The crystallographically inequivalent DF<sub>2</sub><sup>-</sup> ions in NH<sub>4</sub>DF<sub>2</sub> are denoted by (1) and (2); see also Table VI.

our theoretical estimate of 49.5 kHz for the nqcc in the free ion is consistent with the experimental value, the high asymmetry parameter that has been observed in KDF<sub>2</sub> could only be due to solid state effects, static and/or dynamic, since  $\eta$  is necessarily zero for a linear molecule.

In order to estimate the deuterium EFG in the potassium and also the sodium and ammonium bifluorides, we first investigated the static effects of the lattice. We set up a point-charge model for the ions in the crystal, as outlined in Sec. II, and calculated the resulting electrostatic effect on the EFG of a reference DF<sub>2</sub><sup>-</sup> ion. Considering the F...F distances quoted in the Introduction for the bifluorides with monovalent cations, we note, first, that the most obvious effect of the lattice is to slightly reduce the equilibrium F...F distance from our estimated (CPF) gas-phase value. The resulting changes in the deuterium EFG of the unperturbed reference ion, as calculated from Eq. (29), are fairly large; as there are considerable experimental uncertainties in these solid state F...F distances, we can expect substantial errors to be associated with them.

Second, the crystalline environment will affect the intramolecular potential energy function and hence the vibrationally averaged deuterium EFG tensor. While the rigorous calculation of such changes is beyond the scope of the current work, we note that according to the available experimental evidence<sup>12,33-36</sup> the vibrational frequencies in crystalline bifluorides differ typically by a few percent from the gas phase or argon matrix values and, consequently, no major correction is expected to the vibrationally averaged EFG.

### 1. External contributions to the EFG: Point-charge model

The point-charge model we have used in this work is quite a simple one. However, as argued further on, we believe that it is capable of describing the major electrostatic effects of the lattice on a given ion. The bifluoride ion is represented by three point charges, one on each atom, chosen so that the net charge of  $-1e$  and the quadrupole moment of the ion, viz.,  $-6.6311$  a.u. (calculated at the CI-SD level using the [7,5,2,1;5,3,1] basis) are reproduced. This yields a charge of  $+0.430e$  for the hydrogen and  $-0.715e$  for the fluorines. Na<sup>+</sup> and K<sup>+</sup> are represented by charges of  $+1e$ , while for NH<sub>4</sub><sup>+</sup> we use charges of  $+0.2e$  on each atom, as suggested by the x-ray diffraction data of McDonald.<sup>28</sup> Note, however, that in the ammonium salt there are two crystallographically inequivalent types of HF<sub>2</sub><sup>-</sup> (and NH<sub>4</sub><sup>+</sup>) ions which we will denote as types (1) and (2).

The external field-gradient tensor at the deuterium nucleus in the reference DF<sub>2</sub><sup>-</sup> ion was calculated by summing the individual contributions of the point charges that model the appropriate lattice. The convergence of such sums has been found to be quite fast; to obtain results accurate to four decimal figures it was found sufficient to sum over approximately 10 000 unit cells. The results obtained for the sodium, potassium and ammonium bifluorides are presented in Table IV. Comparing the diagonal components of the external EFG tensors for the three bifluoride salts, we note that in sodium bifluoride there is a substantial crystal-field contribution to the total field gradient but only a small anisotropy is predicted. In potassium bifluoride the diagonal components of the EFG tensor are substantially smaller in magnitude than in the sodium salt; however, the  $x$ - $y$  asymmetry in the crystal structure gives rise to an anisotropy in the external field gradient in KHF<sub>2</sub>. It is worth noting at this point that this asymmetry also manifests itself in splitting the degeneracy of the bending-mode frequency of the bifluoride ion<sup>33,78</sup> and in the anisotropy of the proton magnetic shielding tensor.<sup>79</sup> In the ammonium salt the components of the external EFG tensor are smaller still and will contribute little to the total deuterium EFG.

Two questions that naturally arise are: (a) how accurate is the point-charge distribution? and (b) how sensitive is the external EFG to variations in the point charges? In the context of EFG calculations the most stringent test of the point-charge distribution representing the HF<sub>2</sub><sup>-</sup> ions is to calculate quantum mechanically the external EFG due to a single ion at given external points **R**, i.e., according to

$$V_{\alpha\beta} = \langle \Psi | \hat{V}_{\alpha\beta}(\mathbf{R}) | \Psi \rangle, \quad (31)$$

where  $\Psi$  is the wave function of the ion and  $\hat{V}_{\alpha\beta}(\mathbf{R})$  is the EFG operator at **R**, and then to compare the results with the corresponding predictions of the point-charge model. When such comparisons were made at points that correspond to nearest-neighbor separations and orientations of the DF<sub>2</sub><sup>-</sup> ions in KDF<sub>2</sub>, the external EFGs predicted by the point-charge model were within 3%–4% of those calculated by the use of Eq. (31) with a CI-SD wave function and [7,5,2;5,2] basis. At larger distances, corresponding to next nearest-neighbor separations, the agreement, as expected, was found to be even better. Furthermore, test calculations have shown that, as far as the nqcc is concerned, the actual choice of charges representing a bifluoride ion is not critical. For example, in KDF<sub>2</sub>, if the charge on the hydrogen atom is varied from  $0.2e$  to  $0.7e$ , the  $xx$ ,  $yy$ , and  $zz$  components of the

TABLE V. Nonzero components of the Sternheimer shielding constants for  $\text{HF}_2^-$  calculated at the SCF and CI-SD levels of theory using the [7,5,2;5,3] basis at the  $\text{F}\cdots\text{F}$  separation of 2.265 Å.

Shielding constant <sup>a</sup>	SCF	CI-SD
$\gamma_{xx,xx} = \gamma_{yy,yy}$	-0.0343	-0.0476
$\gamma_{xx,yy} = \gamma_{yy,xx}$	0.0597	0.0374
$\gamma_{xx,zz} = \gamma_{zz,xx} = \gamma_{yy,zz} = \gamma_{zz,yy}$	-0.0254	0.0101
$\gamma_{zz,zz}$	0.0508	-0.0203
$\gamma_{xy,xy}$	-0.0470	-0.0425
$\gamma_{xz,xz}$	-0.5562	-0.5779

<sup>a</sup> z axis is the molecular axis.

external field gradient (in a.u.) vary from -0.0040, -0.0059, and 0.0099, respectively, to -0.0013, -0.0105, and 0.0118, provided the symmetry and conservation constraints are maintained. Such variation, while potentially important in the prediction of the asymmetry parameter  $\eta$ , has only a small effect ( $\sim 1$  kHz) on the nqcc. We note that the atomic charges predicted by the Mulliken population analysis,<sup>80</sup> e.g., +0.45e for the charge on hydrogen (from a CI-SD calculation with the [7,5,2;5,3] basis) are consistent with our initial choice. Reducing the ionic character of the crystal by assigning charges to the ions that are smaller in absolute magnitude results in a uniform reduction in the external EFG. For example, for  $\text{KDF}_2$  the use of charges of  $\pm 0.8e$  for the ions reduces the magnitude of the external EFG by  $\sim 20\%$ . As a further test of our point-charge model we carried out population analyses for a  $\text{NaHF}_2$  molecule at the experimental solid state geometry<sup>24</sup> using a SCF wave function generated in a [6,4,1;4,2,1;2,1] basis. The Mulliken analysis<sup>80</sup> predicted a value of +0.89e for the net charge on the sodium atom, while the method of Heinzmann and Ahlrichs<sup>81,82</sup> yielded +0.98e. Our model, consisting of ions with charges of  $\pm 1.0e$  should, therefore, be a reasonable representation of the bifluoride crystals.

## 2. The polarizing effect of the lattice: Sternheimer shielding

As described in Sec. II, the Sternheimer shielding constants for  $\text{HF}_2^-$  were calculated at both the SCF and CI-SD levels of theory using the [7,5,2;5,3] basis. These calculations were performed at the  $\text{F}\cdots\text{F}$  distance of 2.265 Å, i.e., at the experimental geometry in  $\text{NaDF}_2$ . The calculated

shielding constants are listed in Table V. Note that as  $\text{HF}_2^-$  has  $D_{\infty h}$  symmetry, all shielding constants,  $\gamma_{\alpha\beta,\gamma}$ , that describe the change in the EFG due to an external field, vanish identically. This follows from the transformation properties of the shielding tensors:  $\gamma_{\alpha\beta,\gamma}$  transform as the direct products of the appropriate representations  $\Gamma_{\alpha\beta}$  and  $\Gamma_\gamma$  of the EFG tensor and the external electric field, respectively. With one exception ( $\gamma_{xz,xz}$ ) the shielding constants are quite small; thus, the crystal-field induced contributions to the EFG are going to be of minor importance. Consequently, it seems reasonable to use the same set of shielding constants in all the bifluoride salt calculations, and, in particular, to ignore the effects of geometry changes, as test calculations (with a smaller basis) have indicated that the shielding constants are not strongly dependent on the geometry.

Given the external EFGs for the three bifluoride salts and the Sternheimer shielding constants of  $\text{HF}_2^-$  the total EFG at a given deuterium nucleus is readily calculated according to Eq. (11). We assumed the (intramolecular) vibrational correction to be the same as for the gas-phase ion, as, in the absence of accurate information on the potential-energy function for a  $\text{DF}_2^-$  ion in any given crystal lattice, it is not possible to calculate individual ground-state vibrational wave functions. The results for the three bifluoride salts are summarized in Table VI, where for each system we quote the equilibrium EFG for the unperturbed ion [calculated by Eq. (29)], the largest component of the total EFG tensor (incorporating the vibrational and solid state corrections) in the principal-axis system and the resulting nqcc and asymmetry parameter. The uncertainties in the experimental  $\text{F}\cdots\text{F}$  distances introduce corresponding uncertainties in the EFGs and, hence, errors in the nqccs of approximately  $\pm 3$  kHz. Comparing the calculated nqccs and asymmetry parameters we note that, in the case of  $\text{KDF}_2$  our calculations predict a coupling constant that is consistent with the observed value of  $58 \pm 10$  kHz.<sup>15</sup> However, the calculated asymmetry parameter of 0.06 is at serious variance with the experimental value of  $0.4 \pm 0.1$ .<sup>15</sup>  $\text{NaDF}_2$  is predicted to have a substantially larger nqcc than the other salts which is due partly to the large contribution of the crystal lattice to the EFG and partly to the  $\text{F}\cdots\text{F}$  distance being the shortest among the three salts. The asymmetry parameters in all three bifluoride salts are predicted to be uniformly small, ranging from 0.04 to 0.09.

It was noted in the previous section, however, that the

TABLE VI. Deuterium EFGs (equilibrium unperturbed EFG,  $V_{zz}^e$ , and total perturbed<sup>a</sup> EFG in the principal axis system  $V_{zz}$ ), nqccs ( $\chi$ ), and asymmetry parameters ( $\eta$ ) in crystalline sodium, potassium, and ammonium bifluorides.

Crystal	$R_{\text{F}\cdots\text{F}}$ (Å)	$V_{zz}^e$ (a.u.)	$V_{zz}$ (a.u.)	$\chi$ (kHz)	$\eta$
$\text{NaDF}_2$	$2.265 \pm 0.007^b$	$0.067 \pm 0.005$	$0.128 \pm 0.005$	$86.0 \pm 3.4$	$0.04 \pm 0.01$
$\text{KDF}_2$	$2.277 \pm 0.006^c$	$0.058 \pm 0.005$	$0.089 \pm 0.005$	$59.8 \pm 3.4$	$0.06 \pm 0.01$
$\text{NH}_4\text{DF}_2$ (1)	$2.269 \pm 0.005^d$	$0.064 \pm 0.004$	$0.085 \pm 0.004$	$57.1 \pm 2.7$	$0.09 \pm 0.01$
$\text{NH}_4\text{DF}_2$ (2)	$2.275 \pm 0.005^d$	$0.059 \pm 0.004$	$0.081 \pm 0.004$	$54.4 \pm 2.7$	$0.08 \pm 0.01$

<sup>a</sup> Includes corrections for vibrational averaging, external EFG, and Sternheimer shielding.

<sup>b</sup> Reference 24.

<sup>c</sup> Reference 16.

<sup>d</sup> Reference 28.

asymmetry parameter may depend to some extent on the nature of the point-charge distribution; hence this point was investigated further. Varying the charge on the hydrogen atom from  $0.2e$  to  $0.7e$ , while the total charge on the bifluoride ion is fixed at  $-1.0e$ , results in  $\eta$  values in  $\text{KDF}_2$  that vary from 0.02 to 0.10. The corresponding changes in  $\eta$  in the sodium and ammonium bifluorides, however, are  $\leq 0.01$ . If we allow for a decrease in the ionic character of the bifluorides by reducing the total ionic charges to  $\pm 0.9e$  and  $\pm 0.8e$  while maintaining the hydrogen to fluorine charge ratio at  $-0.43/0.715$ , the external field gradients uniformly decrease in absolute magnitude; hence the reductions in the asymmetry parameters are very small ( $\leq 0.01$ ) for all three salts. The reduced ionicity does result in small decreases in the nqccs in the sodium and potassium bifluorides; for the extreme case of  $\pm 0.8e$  these decreases are 5.5 and 1.5 kHz, respectively. We conclude, therefore, that variations in the choice of point-charge distribution will result in only minor variations in the predicted nqccs and asymmetry parameters.

### 3. The polarizing effect of the lattice: Finite-field (point-charge) SCF

The serious discrepancy between the calculated and experimentally observed asymmetry parameters in  $\text{KHF}_2$  prompted us to investigate this system further. We considered the possibility that the polarization of the bifluoride ion and its effect on the deuterium EFG is not predicted sufficiently accurately by the Sternheimer approach we have used. An alternative way of estimating the polarizing effects of the lattice on the bifluoride ion is to calculate the perturbation directly, in the spirit of the finite-field method. We undertook a calculation in which point-charge potential terms representing the lattice were included in the Hamiltonian: the perturbed molecular EFG tensor is then obtained from the corresponding perturbed wave function. The major problem is to establish an accurate representation of the lattice: this should consist of a reasonably small number of ions, but must have the correct convergence for the potential.

The approach we used is based on Evjen's method of computing lattice sums, in particular the Madelung constants of ionic solids.<sup>83,84</sup> Briefly stated, the Evjen method consists of setting up a cell of ions in such a way that it forms a concentric neutral block. The electroneutrality of the cell is achieved by scaling those charges that are on the face, edge, or corner of the block by factors of  $1/2$ ,  $1/4$ , and  $1/8$ , respectively, as such charges contribute to two, four, and eight blocks, respectively. The arrangement of ions for our potassium bifluoride Evjen cell is shown in Fig. 1. The crystal structure is tetragonal ( $I4$ ) and the potassium ions occupy body-centered positions with reference to the bifluoride ions and vice versa. However, the application of the Evjen method to a body-centered structure is not as straightforward as for most other lattices, inasmuch as when calculating the potential at the reference ion two different limits are approached depending on whether the Evjen cells have positive or negative ions in the outermost layer. The true limit is actually the average of the two.<sup>84,85</sup> Consequently, in our implementation of the Evjen method for a body-centered

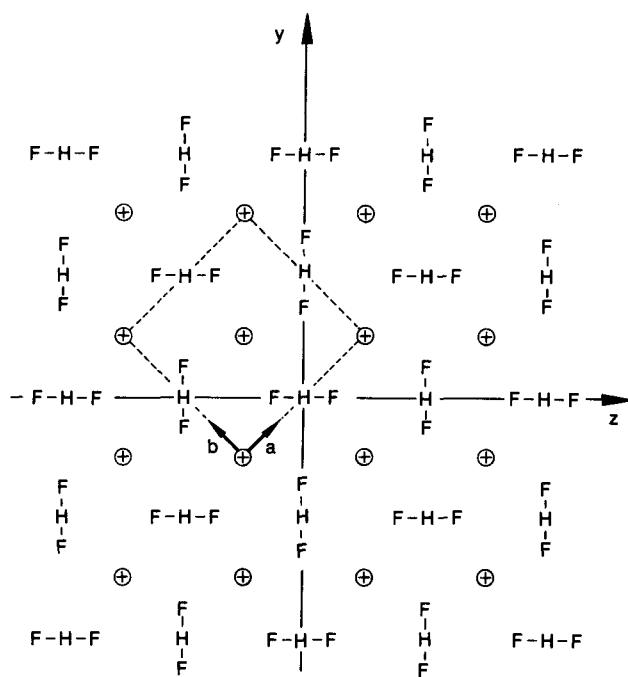


FIG. 1. Two-dimensional projection diagram of the potassium bifluoride crystal structure showing a plane of bifluoride ions ( $x = 0$ ) and a plane of potassium ( $\oplus$ ) ions ( $x = \pm 1/4c$ ). Each bifluoride plane is related to the adjacent one ( $x = \pm 1/2c$ ) by a  $90^\circ$  rotation. The relationship between the molecular  $y,z$  and crystallographic  $a,b$  axes is shown; the  $x$  and  $c$  axes coincide.

structure we scale not only the charges which make up the outermost  $n$ th layer but also the  $n-1$ th. The scaling factors for such a cell are easily shown to be  $1/4$ ,  $1/8$ , and  $1/16$  for the charges on the face, edge, and corner in the  $n$ th layer and  $3/4$ ,  $5/8$ , and  $9/16$  for the corresponding charges in the  $n-1$ th layer. Our model for crystalline  $\text{KHF}_2$  consists of five planes of charges representing the bifluoride ions and four planes of charges, that alternate with the bifluoride planes, representing the potassium ions. Each bifluoride plane contains 25 ions, as shown in Fig. 1, and each potassium layer consists of 16 ions. The point charges that represent the ions are those already used, viz.,  $+1.0e$  for  $\text{K}^+$  and  $+0.43e$  and  $-0.715e$  for the hydrogen and fluorine atoms, respectively, appropriately scaled where required. Such a cell, in fact, reproduces the potential and the external EFG at the central hydrogen atom to better than 1% and the external electric field at the fluorine site to within 4% in comparison with the converged values.

We note at this point that the external EFG at the hydrogen atom has been found to converge fairly rapidly (to the same limit) irrespective of the method of summation. For example, if we use the above scheme without scaling the charges, i.e., relaxing the electroneutrality constraint, the external EFG converges, even though the potential oscillates wildly and appears to diverge as the cell size is changed.

Including the above set of charges representing the Evjen cell in the Hamiltonian of the bifluoride ion we calculated the SCF wave function and the corresponding EFG tensor using the  $[7,5,2;5,3]$  basis. In comparison with the unperturbed ion the changes (in a.u.) in the EFG at the hydrogen atom are 0.0020, 0.0029, and  $-0.0049$  in the  $XX$ ,  $YY$ , and

ZZ components, respectively. Although these corrections are substantially larger than those predicted by the Sternheimer treatment they do not significantly alter our conclusions thus far; the deuterium nqcc is reduced by 3.1 kHz while the anisotropy is very slightly decreased to 0.05.

#### 4. Librational averaging

Next, we consider the effects of librational averaging on the  $^2\text{H}$  nqccs and asymmetry parameters in the crystalline bifluorides. The “*ab initio*” calculation of force fields and librational wave functions for ionic solids such as the bifluoride salts would require a considerable amount of basic theoretical ground work and is beyond the scope of this work. However, we can obtain order of magnitude estimates of the librational effects by utilizing the available experimental estimates of atomic mean-square vibrational amplitudes. For  $\text{KHF}_2$  the fluorine root-mean-square amplitudes of atomic motion  $\langle u_{11}^2 \rangle^{1/2}$  and  $\langle u_{12}^2 \rangle^{1/2}$  have been determined from neutron diffraction experiments to be 0.148 and 0.192 Å, respectively.<sup>16</sup> If we assume that these amplitudes represent reasonable upper bounds for the librational amplitudes, we obtain the figures of 0.017 and 0.028 for  $\langle \theta_x^2 \rangle$  and  $\langle \theta_y^2 \rangle$ , respectively. Substituting these values into Eqs. (27) and (28) we predict a reduction in the principal component of the hydrogen EFG tensor by  $\sim 7\%$  and a contribution of  $\sim 0.02$  to the asymmetry parameter. We must, therefore, conclude that librational averaging can account for only a minute change in the asymmetry parameter in  $\text{KHF}_2$ , unless the mean-square amplitudes are both considerably different and also very large compared with the values we have assumed. As an extreme illustration we consider freezing one mode completely and allowing the other to have the very large root-mean-square amplitude of 0.44 Å ( $\sim 25^\circ$ ). The resulting asymmetry parameter is then  $\sim 0.4$ . However, as discussed in detail by Carrell and Donohue,<sup>17</sup> the atomic amplitudes include the (intramolecular) vibrational as well as translational amplitudes. The root-mean-square librational amplitudes, as deduced by Carrell and Donohue,<sup>17</sup>

are  $5.9^\circ$  for  $\text{NaHF}_2$ ,  $6.5^\circ$  for  $\text{KHF}_2$ , and  $7.8^\circ$  for  $\text{NH}_4\text{HF}_2$ ; moreover, in the potassium and ammonium bifluorides only one librational mode was deemed to be active. Using the above estimates we predict reductions in the deuterium nqccs by 3%, 2%, and 3% in  $\text{NaHF}_2$ ,  $\text{KHF}_2$ , and  $\text{NH}_4\text{HF}_2$ , respectively, and contributions to the asymmetry parameters  $\eta$  of 0, 0.02, and 0.03.

We note at this point that an additional contribution to  $\eta$  in  $\text{KDF}_2$  could arise, namely as a result of the split in the degenerate bending-mode of  $\text{DF}_2^-$ . Using the harmonic approximation and the information contained in Eq. (30), we obtain a value of  $\sim 0.005$  as the contribution to  $\eta$  due to a difference of  $17 \text{ cm}^{-1}$ <sup>33</sup> in the bending frequencies of  $\text{DF}_2^-$ .

#### F. Basis-set incompleteness: An SCF study of the HF molecule

To return to the discussion of basis-set effects: it is apparent from the results of Table II that we have still not reached the SCF limit for the properties of  $\text{HF}_2^-$ . This deficiency is particularly severe for the hydrogen EFG. Hence, in order to get an estimate of the error due to basis-set incompleteness, we have carried out a series of SCF calculations for the HF molecule using a number of extended basis sets including some of the larger ones from Table I. The results, given in Table VII are to be compared with the exact, i.e., numerical SCF, predictions of Sundholm *et al.*<sup>86</sup> We note that the hydrogen EFG calculated for HF using the [6,4,2,1;4,3,2] basis, viz., 0.522 521 a.u., differs from the exact SCF value by  $\sim 0.011$  a.u.; consequently, the SCF limit for the hydrogen EFG in  $\text{HF}_2^-$  may be expected to lie lower than the best calculated value by approximately such an amount. Hence, for the “best” [7,5,2,1;5,4,2] basis we estimate the SCF limit for the hydrogen EFG in  $\text{HF}_2^-$  to be  $0.010 \pm 0.005$  a.u. at the  $\text{F} \cdots \text{F}$  distance of 2.265 Å, while our best correlated [CPF(ED)] estimate (see Table III) becomes  $0.057 \pm 0.005$  a.u.

The question that naturally arises is: what extra functions need to be added to our basis to reproduce the exact

TABLE VII. The total energy ( $E$ ), electric field gradients ( $V_{zz}$ ), dipole moment ( $\mu$ ), and quadrupole moment ( $\theta$ ) (at center of mass) of HF calculated at the SCF level at the interatomic separation of  $1.7328 a_0$  (0.917 Å) using various extended basis sets. All quantities are given in atomic units.

Basis	$E$	$V_{zz}(\text{H})$	$V_{zz}(\text{F})$	$\mu$	$\theta$
[6,4,2,1;4,2,1] <sup>a</sup>	− 100.066 344	0.549 410	2.892 54	0.764 436	1.7179
[6,4,2,1;4,3,2] <sup>a</sup>	− 100.067 078	0.522 521	2.886 61	0.764 418	1.7207
[6,4,3,1;4,3,2] <sup>b</sup>	− 100.067 312	0.520 366	2.869 79	0.762 855	1.7227
[6,4,3,1;4,3,2] <sup>c</sup>	− 100.067 346	0.521 021	2.877 26	0.757 415	1.7311
[6,4,2,1;4,3,2,1] <sup>d</sup>	− 100.067 084	0.522 409	2.888 16	0.764 319	1.7202
[6,4,2,1;4,3,2,1] <sup>e</sup>	− 100.067 103	0.522 643	2.885 59	0.763 097	1.7248
[6,4,2,1;4,3,3] <sup>f</sup>	− 100.067 088	0.518 488	2.890 26	0.764 108	1.7203
[9,7,3,1;5,2,1] <sup>g</sup>	− 100.067 778	0.548 03	2.858 1	0.755 86	1.7284
[14,10,4,2;6,4,2] <sup>h</sup>	− 100.070 6	0.515 8	2.848 4	0.756 6	1.7338
Numerical <sup>i</sup>	− 100.070 82	0.511 927	2.798 78	0.756 076	1.7321

<sup>a</sup> As in Table I.

<sup>b</sup> [6,4,2,1;4,3,2] +  $3d_{\text{F}}$  ( $\zeta = 4.8$ ).

<sup>c</sup> As in b except  $3d_{\text{F}}$  ( $\zeta = 0.2, 0.8, 2.4$ ).

<sup>d</sup> [6,4,2,1;4,3,2] +  $4f_{\text{H}}$  ( $\zeta = 0.5$ ).

<sup>e</sup> [6,4,2,1;4,3,2] +  $4f_{\text{H}}$  ( $\zeta = 0.2$ ).

<sup>f</sup> [6,4,2,1;4,3,2] +  $3d_{\text{H}}$  ( $\zeta = 3.0$ ).

<sup>g</sup> Reference 59.

<sup>h</sup> Reference 87.

<sup>i</sup> Reference 86.

EFG? In an attempt to answer this question we undertook a number of test calculations for HF, as shown in Table VII: we extended the [6,4,2,1;4,3,2] basis by the addition of an extra 3*d* function to the fluorine basis, varied the exponents of the fluorine 3*d* orbitals and added a 4*f* or another 3*d* function to the hydrogen basis. Improving the 3*d* space on fluorine brings the dipole and quadrupole moments into good agreement with the numerical SCF values, marginally improves the EFG on the fluorine atom but has little effect on the hydrogen EFG. The addition of a 4*f* function to the hydrogen basis has only a marginal effect on the EFGs but changes the dipole and quadrupole moments to a considerable extent, probably as a result of the basis becoming slightly unbalanced. Enlargement of the hydrogen 3*d* space further does result in an improved hydrogen EFG; however, the resulting [6,4,2,1;4,3,3] basis is also probably unbalanced, as judged by the poorer quality of the other calculated properties in comparison with the exact SCF predictions. It appears, therefore, that to reach the SCF limit for an EFG, very large well-balanced basis sets, which include extensive sets of polarization functions with angular quantum numbers higher by two than that of the highest strongly occupied atomic orbital, are needed. Since the completion of our work Feller *et al.*<sup>87</sup> have published the results of a very extensive set of SCF and CI studies of one electron properties; their SCF results for HF are reproduced in Table VII. Considering the very large basis set used by Feller *et al.*<sup>87</sup> it is not surprising that their calculated properties are uniformly superior to ours; however, it is worth noting that their hydrogen EFG is still  $\sim 0.004$  a.u. away from the (numerical)

SCF limit. Such an error, while relatively unimportant for most molecules, represents, in the case of  $\text{HF}_2^-$ , a possible basis-set error that would still cause a nearly 10% error in the total coupling constant.

### G. Summary of results

In this section we have presented a large number of relatively complex results. For ease of comprehension and possible future reference, we now summarize our main findings in Table VIII. This table clearly shows the relative magnitudes of the various contributions to the deuterium EFG considered in this paper, both for the free  $\text{DF}_2^-$  ion and the three bifluoride salts, including our error estimates for experimental uncertainties in the  $\text{F}\cdots\text{F}$  distances. As discussed in Sec. III F, we have placed an upper limit of 0.011 a.u. on the hydrogen EFG value in HF due to basis-set incompleteness; consequently, to account for this, all the EFG values for  $\text{DF}_2^-$  in Table VIII could be reduced by approximately such an amount, resulting in a decrease of  $\sim 7$  kHz in the nqcs. We note also that while in  $\text{KDF}_2$  the librational and crystal-field contributions to  $\eta$  are additive, the same is not strictly correct for the ammonium salt. However, as the former are very small, a more rigorous treatment was not attempted; rather, the librally corrected  $\eta$  values for  $\text{NH}_4\text{DF}_2$  should be regarded as possible upper bounds.

### IV. CONCLUSIONS AND FUTURE DIRECTIONS

As foreshadowed in the Introduction, theoretical analysis of the  $^2\text{H}$  nqcs for the bifluoride ion in some simple ionic

TABLE VIII. Summary of calculated deuterium electric field gradients<sup>a,b</sup>  $V_{zz}$ , nuclear quadrupole coupling constants  $\chi$ , and asymmetry parameters  $\eta$ .

System	Calculation	$V_{zz}$ (a.u.)	$\chi$ (kHz)	$\eta$
$\text{DF}_2^-$ (free ion)	SCF ( $R = 2.265 \text{ \AA}$ )	0.020	13	0
	CI-SD(ED) ( $R = 2.265 \text{ \AA}$ )	0.054	36	0
	CPF(ED) ( $R = 2.265 \text{ \AA}$ )	0.067	45	0
	CPF(ED) ( $R_e = 2.283 \text{ \AA}$ )	0.053	36	0
	CPF(ED) ( $R_e = 2.283 \text{ \AA}$ , VC)	0.074	50	0
	CPF(ED) ( $\text{Na}^+ : R = 2.265 \text{ \AA}$ , VC) <sup>c</sup>	0.087	58	0
	CPF(ED) ( $\text{K}^+ : R = 2.277 \text{ \AA}$ , VC) <sup>c</sup>	0.078	52	0
	CPF(ED) ( $[\text{NH}_4^+ (1) : R = 2.269 \text{ \AA}$ , VC] <sup>c</sup> )	0.084	56	0
	CPF(ED) ( $[\text{NH}_4^+ (2) : R = 2.275 \text{ \AA}$ , VC] <sup>c</sup> )	0.079	53	0
$\text{NaDF}_2^d$	CPF(ED) ( $R = 2.265 \text{ \AA}$ , VC, CFS)	0.128	86	0.04
	CPF(ED) ( $R = 2.265 \text{ \AA}$ , VC, CFS, LC)	0.124	83	0.04
$\text{KDF}_2^d$	CPF(ED) ( $R = 2.277 \text{ \AA}$ , VC, CFS)	0.089	60	0.06
	CPF(ED) ( $R = 2.277 \text{ \AA}$ , VC, CFF)	0.084	56	0.05
	CPF(ED) ( $R = 2.277 \text{ \AA}$ , VC, CFF, LC)	0.082	55	0.07
$\text{NH}_4\text{DF}_2 (1)^d$	CPF(ED) ( $R = 2.269 \text{ \AA}$ , VC, CFS)	0.085	57	0.09
	CPF(ED) ( $R = 2.269 \text{ \AA}$ , VC, CFS, LC)	0.082	55	0.12
$\text{NH}_4\text{DF}_2 (2)^d$	CPF(ED) ( $R = 2.275 \text{ \AA}$ , VC, CFS)	0.081	54	0.08
	CPF(ED) ( $R = 2.275 \text{ \AA}$ , VC, CFS, LC)	0.079	53	0.11

<sup>a</sup> All calculations using the [7,5,2,1;5,4,2] basis.

<sup>b</sup> VC  $\equiv$  with vibrational correction; CFS  $\equiv$  with crystal-field correction using Sternheimer method; CFF  $\equiv$  with crystal-field correction using finite-field (point-charge) method; LC  $\equiv$  with librational correction (Ref. 17).

<sup>c</sup>  $\text{M}^+ : R$  = experimental  $\text{F}\cdots\text{F}$  distance in the  $\text{MDF}_2$  salt.

<sup>d</sup> Error estimates of  $\sim 3$  kHz in  $\chi$  due to experimental uncertainties in the  $\text{F}\cdots\text{F}$  distances; see Table VI.

solids has proved to be quite complex. Although we have considered all possible contributions to the hydrogen EFG in the crystal environment, our calculations do not indicate a value for the asymmetry parameter significantly greater than zero; thus, we are in disagreement with the result of Blinc *et al.* However, our result for the nqcc in  $\text{KDF}_2$  ( $55 \pm 3$  kHz) is in agreement with that of Blinc *et al.*, and we have established that the sign of the nqcc is positive. In addition, we have predicted nqcc and  $\eta$  values for  $\text{NaDF}_2$  and  $\text{ND}_4\text{DF}_2$ , salts with crystal forms different from  $\text{KDF}_2$  and each other, and for which no experimental nqcc data are available.

In the light of the experimental data for a variety of bifluoride salts in different crystal forms reviewed in the Introduction, and our present findings on the dependence of the solid state  $^2\text{H}$  nqcc on both the crystal-field strength and symmetry, we can make a number of suggestions for further experimental work. First, our work points to the need for further  $^2\text{H}$  nqcc work on the simple bifluoride salts with monovalent cations, both to test our predictions regarding the effects of differing crystal symmetry (e.g., the series  $\text{KDF}_2$ ,  $\text{NaDF}_2$ , and  $\text{ND}_4\text{DF}_2$ ), and to test the effects of varying crystal-field strength for a fixed symmetry (e.g., the series  $\text{KDF}_2$ ,  $\text{RbDF}_2$ , and  $\text{CsDF}_2$ ). Second,  $^2\text{H}$  nqcc results for the more complex alkali earth mixed bifluoride salts and hydrazinium salt, for which some structural data are available,<sup>22,26,27,32</sup> would be interesting. Moroz *et al.*<sup>27</sup> have observed that, in these salts, a given  $\text{F}\cdots\text{F}$  distance may be associated with either a symmetric or asymmetric H bond; thus the potential well for the proton depends not only on the  $\text{F}\cdots\text{F}$  distance but also the strength and symmetry of the external crystal field. This is qualitatively different from the isolated-ion case where we might expect asymmetric H bonds to be favored at greater  $\text{F}\cdots\text{F}$  distances.

Our analysis has also identified some deficiencies and uncertainties in the theoretical treatment which limit its accuracy and merit further study. First, we have demonstrated a general basis-set limit problem for representing molecular EFGs; this is peculiarly extreme for the case of hydrogen EFGs in the bifluoride ion, and, by extension, is expected to be similarly serious in other symmetrically H-bonded systems. Additional uncertainties in our theoretical model arise from the treatment of crystal-field effects in the solids. As reoptimization of the bifluoride-ion geometry in the perturbing environment of specific crystal fields was not feasible computationally in this study, we have used available experimental geometries and taken into account the effect on the EFGs of the reported errors; this procedure has limited the number of solids for which we were able to make nqcc predictions. Similarly, as we were not able to calculate the molecular potential in the presence of given perturbing crystal fields, we have used the potential for the free ion in calculating the vibrationally averaged contribution to the EFGs in the solids; we do not expect this assumption to introduce significant errors into our predictions. However, in view of the crystal structure and vibrational experimental data for the different solids summarized in the Introduction and above, theoretical study of the bifluoride-ion potential in the presence of perturbing crystal fields may be a worthwhile

exercise. Lastly, our simple point-charge model, which is purely an electrostatic model and does not allow for charge transfer and which has been used for calculating the static and induced crystal-field contributions to the EFG, is subject to a number of uncertainties as discussed in the paper. The final uncertainty in our theoretical treatment is that for librational effects; while we have been able to provide only estimates for these effects, our arguments suggest that they are relatively minor contributors to the total hydrogen EFG.

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