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A test of *ab initio*-generated, radial intermolecular potential energy functions for five axially-symmetric, hydrogen-bonded complexes B···HF, where B = N_2, CO, PH_3, HCN and NH_3

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The radial potential energy functions for five axially symmetric, hydrogen-bonded complexes B···HF (B = N_2, CO, PH_3, HCN and NH_3) have been calculated *ab initio* at the explicitly correlated level of theory CCSD(T)(F12c)/cc-pVTZ-F12 as a function of the hydrogen-bond distance r(Z···H), where Z is the hydrogen-bond acceptor atom of B. The remaining geometric parameters were optimised at each point in the calculation. The functions so generated were then used to estimate the spectroscopic constants ω_σ, $\omega_\sigma x_\sigma$,α_σ, and the $v_\sigma = 1 \leftarrow 0$ transition wavenumber associated with the intermolecular stretching mode ν_σ of each B···HF by using two equivalent approaches. Both involved the assumption that the vibrational modes of the B and HF molecules were sufficiently stiff relative to the intermolecular stretching mode that B···HF could be treated in a pseudo-diatomic approximation. One approach used derivatives of the potential evaluated at the distance $r = r_e$ while the other used the potential constants obtained by non-linear regression fits of three analytical functions (Morse, Rydberg and Hulburt–Hirschfelder) to the *ab initio* calculated points. The two approaches would give exactly the same results if the functions were a perfect fit. The H–H function gave the best fit. The determined spectroscopic constants were found to be in reasonable agreement with the limited number available by experiment. The efficacy of the approach was tested for the diatomic molecule $H^{35}Cl$ by taking advantage of both an accurate RKR-type potential and an accurate set of spectroscopic constants. It was also established that the relationship $D_e = k_\sigma/(2a^2)$ between two measures (D_e and k_σ, both calculated *ab initio*) of the strength of the hydrogen bond in the B···HF complexes (and required if the H–H function were an accurate representation of the B···HF potential functions) holds to an excellent level of approximation, and supports the conclusion that this function is appropriate to represent the hydrogen bond in the complexes investigated.

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1. Introduction

The aim of this article is to examine the radial potential energy function, that is the variation of the energy as a function of intermolecular distance, for some simple hydrogen-bonded complexes in the family B···HF, where B is a simple Lewis base. These functions will be calculated *ab initio* at a good level of theory, that is the CCSD(T)-F12c/cc-pVTZ-F12 level, which gives equilibrium dissociation energies D_e not too far from the complete basis set limit. The PE functions thereby obtained will then be fitted, *via* non-linear regression, to three simple analytical functions (initially proposed for diatomic molecules but used here with the internuclear distances of the diatomic molecules replaced by the intermolecular distances of the weakly bound complexes), namely the Morse function,[1] the Rydberg function[2] and the Hulburt–Hirschfelder (H–H) function.[3] The aim is to find which gives the most accurate fit and therefore which is best as a model function for the Z···H hydrogen bond. The forms of these functions are given in eqn (1)–(3) for the Morse, Rydberg, and Hulburt–Hirschfelder versions, respectively.

$$V(x) = D_e[1 - e^{-ax}]^2 \tag{1}$$

$$V(x) = D_e - D_e[1 + bx]e^{-bx} \tag{2}$$

$$V(x) = D_e[(1 - e^{-ax})^2 + ca^3x^3e^{(-2ax)}(1 + abx)] \tag{3}$$

in which a, b and c are constants, $x = (r - r_e)$, r_e is the equilibrium internuclear distance Z···HF (Z is the acceptor atom in B) and D_e is the equilibrium dissociation energy for the process B···HF = B + HF.

The hydrogen-bonded systems investigated were chosen for their simplicity and, importantly, because each is either a linear or a symmetric-top molecule with HF lying along the unique axis at equilibrium. This ensures that for each B···HF there is a

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clearly defined path along the extension of the symmetry axis that leads to dissociation into B and HF. The complexes selected were $N_2\cdots HF$,[4–6] $OC\cdots HF$,[7–9] $H_3P\cdots HF$,[10] $HCN\cdots HF$[11–13] and $H_3N\cdots HF$.[14] Each has been investigated spectroscopically in isolation in the gas phase, all by rotational spectroscopy and some by high-resolution vibration–rotation spectroscopy, as revealed in the cited papers. The most fully examined is $HCN\cdots HF$ and it is this complex for which the calculations presented here are best tested by comparing a number of spectroscopically determined constants with those calculated from the analytical potential energy functions fitted to the numerical version obtained *ab initio*. It was noted[15,16] previously that D_e for such complexes is, to reasonable approximation, directly proportional to the intermolecular stretching quadratic force constant k_σ This is in fact a necessary consequence of all three functions if the constants a of Morse and Hulburt–Hirschfelder and b of Rydberg functions, do not vary much from molecule to molecule.

The fitting procedure and the level of theory used for the $B\cdots HF$ complexes will be tested initially against the accurate experimental potential energy function of the Rydberg-Klein Rees type for $H^{35}Cl$ as determined by Coxon and Hajigeorgiou.[17]

2. Theoretical methods

The energy of each of the complexes $N_2\cdots HF$, $OC\cdots HF$, $H_3P\cdots HF$, $HCN\cdots HF$ and $H_3N\cdots HF$ was calculated as a function of the distance r between the nucleus of acceptor atom Z of B and the proton of HF in increments of 0.05 Å, with either $C_{\infty v}$ or C_{3v} symmetry, as appropriate, maintained throughout. The calculations were carried out by using the MOLPRO package[18,19] and employed the explicitly correlated CCSD(T)-F12c level of theory[20,21] with cc-pVTZ-F12 basis functions.[22] Tests using the counterpoise keyword showed that basis set superposition error (BSSE) is very small for such calculations. For example, the change in D_e for $H_3N\cdots HF$ (the most strongly bound member of the series by far) from this source was only 0.6 kJ mol^{-1}. Accordingly, BSSE corrections to the potential function calculations were not made. The calculation of the PE function for HCl was truncated at $r = 3.2$ Å to avoid spin contamination problems that occur as the Coulson–Fisher point[23] in the internuclear distance is approached and thereby to allow the same level of theory to be used for all calculations reported here.

The intermolecular quadratic force constant k_σ was obtained for each complex $B\cdots HF$ by fitting the potential energy curve $V(r - r_e)$ *versus* $r - r_e$ within ±0.1 Å of the equilibrium intermolecular distance r_e by a sixth-order polynomial and then evaluating the second derivative with respect to $(r - r_e)$ at $r = r_e$.

3. Results

3.1 A test of the Morse, Rydberg and Hulburt–Hirschfelder functions with the RKR potential function of $H^{35}Cl$

A very accurate potential energy function for $H^{35}Cl$ has been evaluated by Coxon and Hajigeorgiou[17] by using the RKR method to give the energies at the classical turning points of the vibration for the vibrational states $v = 0$ to $v = 20$, the latter lying within only 18 cm^{-1} of the dissociation limit at $D_e = 445.39$ kJ mol^{-1} (37232.0 cm^{-1}). This potential energy $V(r - r_e)$ is plotted against $(r - r_e)$, where $r_e = 1.27454677(6)$ Å,[17] in Fig. 1. The open circles mark the energies at the turning points. Also shown in Fig. 1 are the non-linear regression fits to the RKR points by a Morse function (dashed line) and a Rydberg function (continuous green line). It is clear that the Rydberg function gives a better fit than the Morse function, but that both functions begin to diverge from the RKR-type points beyond $r = r_e$ and this becomes more significant beyond $(r - r_e) > 1$ Å. The constants D_e, a and b that result from these fits are recorded in Table 1 together with their standard errors. The largest residuals are: 9.1 kJ mol^{-1} for the Rydberg function fit and 12.0 kJ mol^{-1} for the Morse function fit. Also included in Table 1 are the values of D_e and r_e for $H^{35}Cl$ determined by Coxon and Hajigeorgiou.[17] It is clear from Table 1 that both analytical functions overestimate D_e by about 2–5%. Fig. 2 shows the corresponding diagram for the fit of the $H^{35}Cl$ RKR- type data by the Hulburt–Hirschfeldr function. The continuous green curve is the fitted H–H function.

The determined parameters D_e, a, b and c from the non-linear regression fit are included in Table 1. All fitted points except the final one at $(r - r_e) = 3.5$ Å have residuals lying in the range ±5 kJ mol^{-1} for the H–H function fit, confirming its superior quality. This is reinforced by the standard errors of fitted parameters and R^2, which is the usual goodness-of-fit measure for regression analyses, (see Table 1).

3.2 A fit of the Morse, Rydberg and Hulburt–Hirschfelder functions to the potential energy curve of HCl calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory

Having tested the three types of analytical potential energy function with the aid of the high-quality RKR-type $H^{35}Cl$ experimental function, the version obtained *ab initio* by calculation at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory

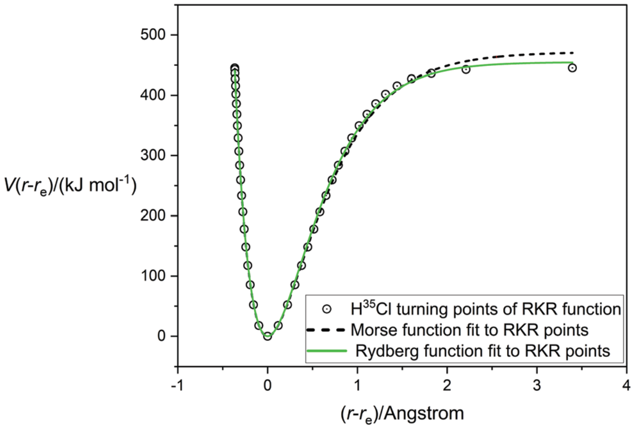

Fig. 1 The RKR-type potential energy function for $H^{35}Cl$ due to Coxon and Hajigeorgiou[17] (open circles) fitted by a Morse function (dashed line) and a Rydberg function (green line).

Table 1 Parameters of the Morse, Rydberg and Hulburt–Hirschfelder function fits to the Coxon–Hajigeorgiou RKR-type potential energy function[a] for $H^{35}Cl$

Parameter	Morse function	Rydberg function	Hulburt–Hirschfelder function
D_e/(kJ mol^{-1})	471.9(25)	454.8(1.7)	455.1(1.7)
a/Å^{-1}	1.854(5)	—	1.838(8)
b/Å^{-1}	—	2.704(5)	3.51(68)
c	—	—	0.042 (7)
R^2	0.9982	0.9991	0.9997

[a] The best available value of D_e for $H^{35}Cl$ is 445.39 kJ mol^{-1}, with r_e = 1.27454677(6) Å from ref. 17.

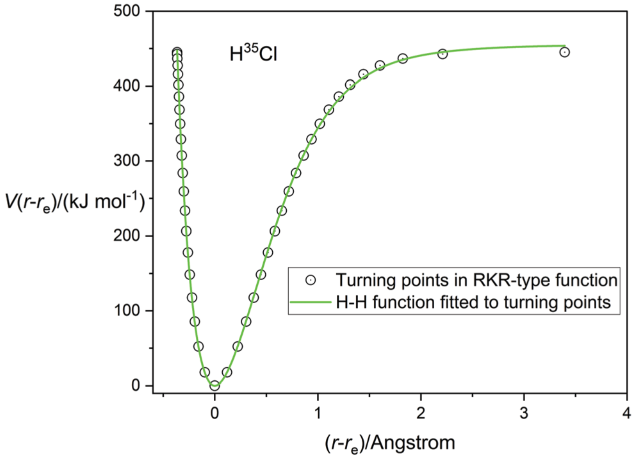

Fig. 2 The RKR-type potential energy function for $H^{35}Cl$ due to Coxon and Hajigeorgiou[17] (open circles) fitted by a Hulburt–Hirschfelder function (continuous green line).

can be similarly scrutinized. Fig. 3 display this function, with points calculated every 0.05 Å in the range $(r - r_e) = -0.4$ to 1.8 Å and indicated by the open circles. The green continuous line again represents the non-linear regression fit of the Hulburt–Hirschfelder function to these points. The parameters of the fit are included in Table 2, together with those derived from the corresponding fits of the Morse function and the Rydberg function to the same calculated points. Recall that the CCSD(T)(F12c) calculation was not extended beyond $(r - r_e) = 1.8$ Å to avoid the effects of spin contamination that begin at the Coulson-Fischer point. Fig. 3 indicates that the Hulburt–Hirschfelder function provides a good fit to the *ab initio* calculated points. As with the fits to the RKR-type points for $H^{35}Cl$, the obtained parameters for the Morse and Rydberg functions were less precise, as indicated by the R^2 values. It is clear from Table 2 that although the D_e values have similar errors for all three analytical functions, those values are higher than the best experimental value from ref. 17. Fig. 4 makes the direct comparison of the RKR-type points for $H^{35}Cl$ with those calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level and illustrates visually that the *ab initio* potential function is in excellent agreement with the best available function.

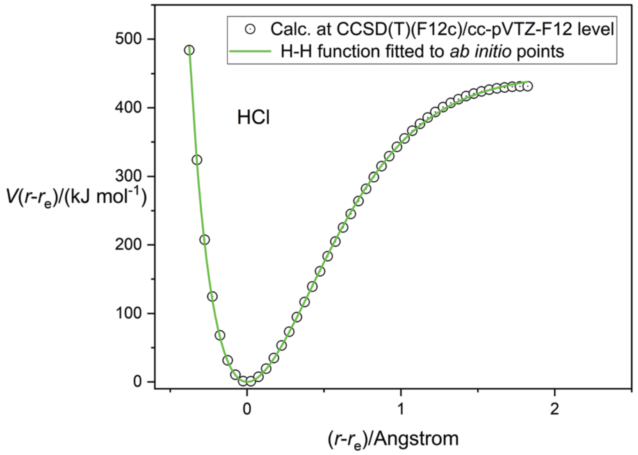

Fig. 3 The potential energy function of HCl calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory (open circles) fitted by the Hulburt–Hirschfelder analytical function (continuous green line).

Table 2 Parameters of the Morse, Rydberg and Hulburt–Hirschfelder function fits to the potential function of HCl calculated *ab initio* at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory

Parameter	Morse function	Rydberg function	Hulburt–Hirschfelder function
D_e/(kJ mol^{-1})	484.4(16)	461.4(17)	455.3(24)
a/Å^{-1}	1.848(4)	—	1.818(8)
b/Å^{-1}	—	2.710(7)	4.37(78)
c	—	—	0.045(7)
R^2	0.9993	0.9991	0.9997

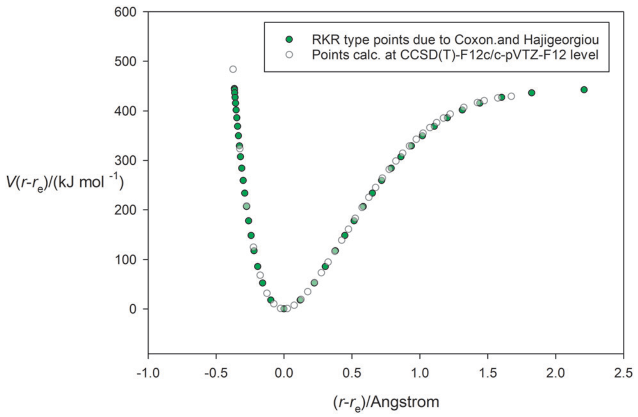

Fig. 4 Comparison of the potential energy curve for HCl calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level (unfilled circles) and that of the RKR-type due to Coxon and Hajigeorgiou[17] (green-filled circles).

3.3 Calculation of spectroscopic properties of $H^{35}Cl$ from the RKR-type and CCSD(T)(F12c)/cc-pVTZ-F12 potential energy functions using derivatives of $V(r - r_e)$ with respect to r, evaluated at $r = r_e$

It can be shown[24] that, for diatomic molecules, the equilibrium spectroscopic wavenumbers ω_e, and $\omega_e x_e$ and the vibration–rotation constant α_e are related to various derivatives of the potential energy function $V(r - r_e)$ by eqn (4)–(6):

$$\omega_e = (2\pi c)^{-1}[V''(r_e)/\mu]^{\frac{1}{2}} \tag{4}$$

$$\omega_e x_e = \left(\frac{\hbar}{\pi c \mu}\right)\left\{\frac{5}{96}\left[\frac{V'''(r_e)}{V''(r_e)}\right]^2 - \frac{1}{32}\left[\frac{V''''(r_e)}{V''(r_e)}\right]\right\} \tag{5}$$

$$\alpha_e = -\left[\frac{V'''(r_e)}{3V''(r_e)}r_e + 1\right]6\frac{B_e^2}{\omega_e} \tag{6}$$

In these equations, V'' is the second derivative of the potential function with respect to r evaluated at r_e, and so on, μ is the reduced mass of the diatomic molecule and c is the speed of light. The various derivatives were determined by fitting the points, calculated at 0.05 Å intervals, between 0.2 and −0.2 Å with a 7th order polynomial and differentiating the result with respect to r. The resulting values of ω_e, $\omega_e x_e$ and α_e are given in Table 3 for the diatomic molecule $H^{35}Cl$, both for the potential energy function of the RKR type due to Coxon and Hajigeorgiou[17] and for that calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level. The purpose of this approach is to provide a calibration in the case where the equations are applied to a diatomic molecule. Experimental values of ω_e, $\omega_e x_e$ and α_e for $H^{35}Cl$ are accurately known[26] and are reproduced in Table 3. It is clear from Table 3 that, as expected, the Coxon–Hajigeorgiou RKR-type function leads to almost perfect reproduction of the experimental values of ω_e, $\omega_e x_e$ and α_e for $H^{35}Cl$. The *ab initio* calculated function also yields reasonably good agreement with the experimental values of ω_e and $\omega_e x_e$ but significantly underestimates α_e.

3.4 Calculation of spectroscopic properties of the five complexes B···HF available from their CCSD(T)(F12c)/cc-pVTZ-F12 potential energy functions by using derivatives of $V(r - r_e)$ with respect to r, evaluated at $r = r_e$

The potential energy curves $V(r - r_e)$ *versus* $(r - r_e)$ for the five complexes B···HF (B = N_2, CO, PH_3, HCN and NH_3) calculated *ab initio* at the CCSD(T)(F12c)/ccpVTZ-F12 level are collected together in Fig. 5. The points, which were calculated at 0.05 Å intervals in r with geometry optimization at each, are not shown explicitly but are connected by a spline function to give continuous curves for clarity. The dissociation energies cover the range from ∼50 kJ mol^{-1} (H_3N···HF) to ∼10 kJ mol^{-1} (for N_2···HF). The spectroscopic properties ω_e, $\omega_e x_e$ and α_e for the five complexes can be estimated by use of eqn (4)–(6), respectively. The required derivatives V'' *etc.* were obtained by the method used for $H^{35}Cl$, but a fit to a 6th order polynomial was sufficient. In applying eqn (4)–(6) to the B···HF complexes, there is an implicit assumption that the component molecules B and HF are sufficiently rigid, relative to the intermolecular hydrogen bond of the complexes examined, for these equations can be applied if $\mu = (m_B m_{HF})/(m_B + m_{HF})$ is used in place of the diatomic molecule reduced mass. In that case, the determined properties are written as ω_σ, $\omega_\sigma x_\sigma$ and α_σ where the subscripts now indicate that they refer to the intermolecular stretching mode ν_σ of the complexes. This assumption is reasonable given the simplicity of the complexes and the large vibrational wavenumbers of B and HF compared with those calculated for the hydrogen-bond stretching mode ν_σ. The results obtained under this assumption are included in Table 3. Their comparison with such experimental quantities as are available for the B···HF will be postponed until Section 3.4.

3.5 The fit of the Morse, Rydberg and Hulburt–Hirschfelder functions to the potential energy curves of the B···HF calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory

The three analytical potential energy functions tested for HCl were next fitted to the *ab initio* calculated points for each of the five axially symmetric hydrogen-bonded complexes B···HF. The fits of each of the three functions (Morse, Rydberg and Hulburt–Hirschfelder) to the *ab initio* calculated points for HCN···HF are displayed in Fig. 6(a)–(c), respectively. The quality of fit to the Rydberg function is worse than that of the Morse function. As found for HCl, the Hulburt–Hirschfelder function provides the best fit to the CCSD(T)(F12c)/cc-pVTZ-F12 calculated points. This is clear from Table 4, which records the

Table 3 Spectroscopic properties associated with vibration in $H^{35}Cl$ and with the intermolecular stretching mode of the axially symmetric hydrogen-bonded complexes B···HF, where B = N_2, CO, PH_3, HCN and NH_3. These properties were calculated from the derivatives of the $V(r - r_e)$ function, the latter calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory, in each case. For $H^{35}Cl$, those obtained from the RKR-type function and experiment are also included

	Spectroscopic property					
Complex	B_e/MHz (calc.)[a]	r_e[a]/Å	ω_σ[b]/cm^{-1}	$\omega_\sigma x_\sigma$[b]/cm^{-1}	α_σ[b]/MHz	$\nu = 1 \leftarrow 0$ wavenumber/cm^{-1}
$H^{35}Cl$ (experiment)	317582.622	1.274552[c]	2990.946[c]	52.8186[c]	9209.1[c]	2885.31
$H^{35}Cl$ (RKR)	317582.622	1.274552	2991.1	53.2	9190.0	2884.0
$H^{35}Cl$ (*ab initio*)	316880.128	1.275964	2999.6	51.6	9127.5	2896.4
N_2···HF	3302.814	2.087212	115.4	4.66	51.4	106.1
OC···HF	3125.996	2.090646	132.7	3.98	35.4	124.7
H_3P···HF	3550.382	2.362105	134.2	2.97	45.9	128.3
HCN···HF	3619.792	1.853759	181.5	3.99	28.9	173.5
H_3N···HF	7437.592	1.699216	254.0	4.19	59.3	245.6

[a] Calculated from the geometry optimised at the CCSD(T)(F12c)/cc-pVTZ-F12 level, except for $H^{35}Cl$ (RKR), which uses the experimental values of r_e and B_e from ref. 25. [b] The subscript e (rather than σ) is appropriate for $H^{35}Cl$ quantities. [c] See ref. 25 for a collection of experimentally observed constants for $H^{35}Cl$.

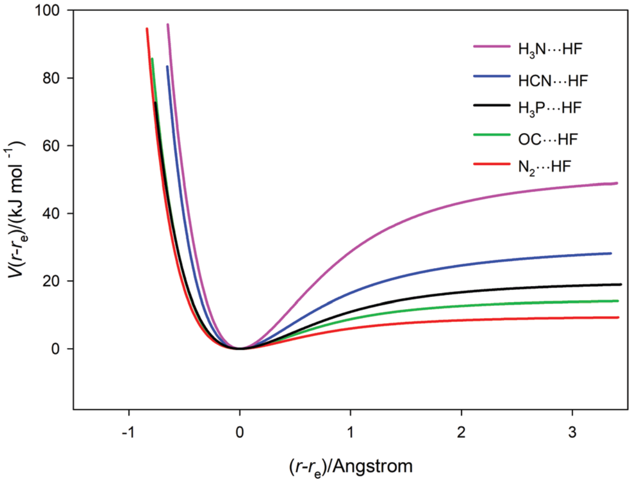

Fig. 5 Potential energy curves $V(r - r_e)$ *versus* $(r - r_e)$ for the five hydrogen-bonded complexes $B\cdots HF$ (B = N_2, CO, PH_3, HCN and NH_3) calculated at 0.05 Å intervals, with geometry optimization at each point. The points (not shown explicitly) are joined by a spline function.

parameters obtained from a non-linear regression fit for each $B\cdots HF$ complex to each of the 3 analytical functions.

In applying the Morse, Rydberg and Hulburt–Hirschfelder functions, all of which were proposed originally for diatomic molecules, to the five complexes $B\cdots HF$, the assumption is again that the B and HF molecules are sufficiently rigid relative to the intermolecular hydrogen bond to allow the complexes to be treated in reasonable approximation as diatomic molecules. The fact that in each case the intermolecular non-covalent bond lies along the symmetry axis is a useful simplification. Fig. 7 compares the potential energy curve for $HCN\cdots HF$, calculated as a function of the $(r - r_e)$ (applying geometry optimization at each point), with that calculated when HCN and HF are frozen at the geometries they possess in the optimized equilibrium version of the complex. Both curves were calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level. It is clear that, apart for small differences on the repulsive part of the curves at small distance $r(N\cdots F)$, the two sets of points are almost coincident for $(r - r_e) > -0.7$ Å and *de facto* lie very close to the H–H fit to the relaxed function shown in Fig. 6(c).

To decide which, if any, of the three analytical potential energy functions is suitable as a model for the hydrogen bond in these axially symmetric complexes $B\cdots HF$, one criterion must be the goodness of their fits to the *ab initio*-calculated functions. However, another important criterion is how well the fitted analytical functions predict spectroscopic properties associated with the intermolecular stretching mode σ, namely the equilibrium stretching wavenumbers ω_σ and $\omega_\sigma x_\sigma$, the vibration–rotation constant α_σ and the dissociation energy D_e, all of which can in principle be measured spectroscopically. $HCN\cdots HF$ is the most investigated of the five complexes $B\cdots HF$ selected for consideration here, but some of the spectroscopic constants are also available for $OC\cdots HF$ and $N_2\cdots HF$. Eqn (4)–(6), as set out in Section 3.2, allow ω_σ, $\omega_\sigma x_\sigma$ and α_σ, respectively, to be obtained from the fitted parameters of each of the three analytical potential functions for each of the five complexes $B\cdots HF$. As indicated earlier, these equations involve derivatives of the potential function with respect to r when evaluated at $r = r_e$. It has been established that the Hulburt–Hirschfelder function gives a better fit to the potential energy curves of the five $B\cdots HF$ complexes obtained through *ab initio* calculations at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory. Therefore, only the relationships between a, b and c of this function and ω_σ, $\omega_\sigma x_\sigma$ and α_σ, will be considered here.

The results of evaluating eqn (4) and (5) for the Hulburt–Hirschfelder function are as follows:

$$k_\sigma = 2a^2 D_e, \tag{7}$$

$$\omega_\sigma = \frac{1}{2\pi c}\left(\frac{k_\sigma}{\mu}\right)^{\frac{1}{2}} = \frac{1}{2\pi c}\left(\frac{2a^2 D_e}{\mu}\right)^{\frac{1}{2}} \tag{8}$$

$$\omega_\sigma x_\sigma = \frac{\hbar a^2}{4\pi c\mu}\left[\frac{15(c-1)^2}{8} - \frac{7}{8} + \frac{3c}{1} - \frac{3bc}{2}\right] \tag{9}$$

Eqn (9) transforms to the corresponding expression obtained from the Morse function (see ref. 23) when $b = c = 0$, as required.

It can be shown[3,26] by use of eqn (6) that the vibration–rotation constant α_e for a diatomic molecule is related to the constants a and c of the Hulburt–Hirschfelder potential energy function by

$$\alpha_e = 6\frac{{B_e}^2}{\omega_e}[ar_e(1-c)-1], \tag{10}$$

where B_e is the equilibrium rotational constant. If the components B and HF of the complex can be assumed rigid and eqn (10) is applied in that approximation, a route to α_σ is available because B_e is known from the *ab initio* calculations described here. Table 5 gives the values of ω_σ, $\omega_\sigma x_\sigma$, α_σ, and the $\nu_\sigma = 1 \leftarrow 0$ transition wavenumber for the hydrogen-bond stretching mode ν_σ. They were calculated from eqn (8)–(10) using the parameters a, b, c of the Hulburt–Hirschfelder function (see Table 4) obtained by fitting the *ab initio*-generated potential energy curves for each of the five $B\cdots HF$. Also in Table 5 are the corresponding quantities for $H^{35}Cl$ calculated (1) from fit of the H–H function to the Coxon–Hajigeorgiou RKR-type function,[17] and (2) from the fit of the H–H function to the CCSD(T)(F12c)/ccpVTZ-F12 points calculated here. The experimental values of the $H^{35}Cl$ properties are also included in Table 5 for convenience.[25] The agreement of these quantities with those obtained by fitting the RKR-type potential with the H–H function (see Table 3) is reasonable, although D_e is overestimated by about 2% while ω_e is underestimated by 0.5%. As might be expected the terms $\omega_e x_e$ and α_e for $H^{35}Cl$, which account for differences between equilibrium and zero-point vibrational and rotational constants, respectively, are more significantly in error, by 5% and 9%. The set of quantities for $H^{35}Cl$ calculated from the potential energy function generated *ab initio* and fitted by the H–H function, also given in Table 4, are somewhat more in error, as might be expected.

The spectroscopic constants of the $B\cdots HF$ have been estimated by two equivalent approaches, both of which depend

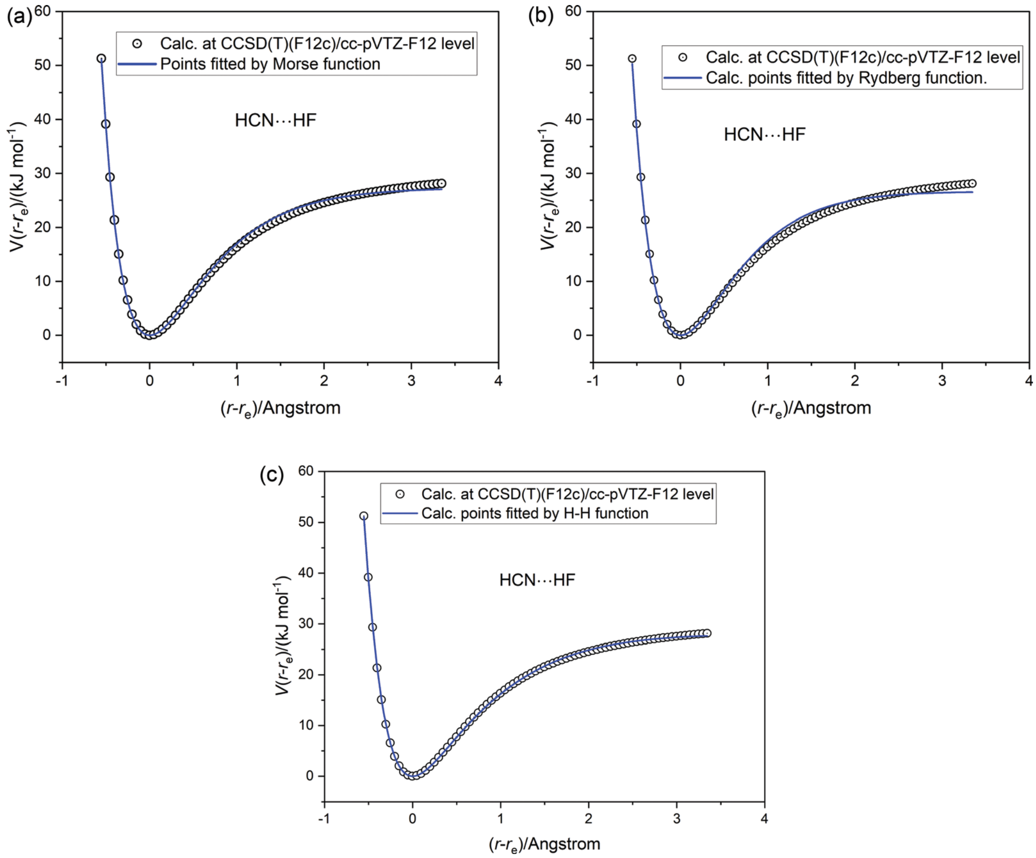

Fig. 6 Potential energy $V(r - r_e)$ *versus* $(r - r_e)$ for HCN···HF calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level (open circles). The continuous blue line is a non-linear regression fit to the *ab initio* calculated points by (a) a Morse function (b) a Rydberg function and (c) a Hulburt–Hirschfelder function. The parameters of the fits are included in Table 4.

Table 4 Constants of the Morse, Rydberg and Hulburt–Hirschfelder analytical potential energy functions obtained by fitting the $V(r - r_e)$ *versus* $(r - r_e)$ points generated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory for axially-symmetric complexes B···HF

	Morse function		Rydberg function		Hulbert–Hirschfelder function			
Complex	D_e/(kJ mol^{-1})	a/Å^{-1}	D_e/(kJ mol^{-1})	b/Å^{-1}	D_e/(kJ mol^{-1})	a/Å^{-1}	b	c
N_2···HF	9.07(2)	1.740(2)	8.84(4)	2.557(3)	9.20(1)	1.720(5)	0.90(7)	−0.067(4)
OC···HF	13.96(5)	1.583(2)	13.56(5)	2.334(3)	14.02(2)	1.603(3)	1.29(10)	−0.035(3)
H_3P···HF	18.87(3)	1.441(2)	18.35(6)	2.101(3)	19.02(2)	1.447(2)	1.69(12)	−0.026(3)
HCN···HF	27.35(9)	1.556(4)	26.64(14)	2.263(11)	28.04(5)	1.545(5)	1.20(9)	−0.084(4)
HCN···HF[a]	—	—	—	—	28.21(5)	1.581(7)	0.76(9)	−0.120(5)
H_3N···HF	49.92(17)	1.354(3)	48.41(12)	1.977(4)	49.21(7)	1.440(3)	−1.14(16)	0.042(3)

[a] The values in this row refer to the Hulburt–Hirschfelder function fitted to the *ab initio* potential energy points generated with the HCN and HF geometries frozen at their values in the equilibrium complex (see text for discussion).

ultimately on eqn (4)–(6). Those in Table 3 result from the application of eqn (4)–(6) directly, while those in Table 5 were obtained by first fitting the H–H function to the *ab initio* calculated points and then applying eqn (8)–(10). If the H–H function were a perfect fit to the *ab initio* points, the two sets of values for the B···HF in Tables 3 and 5 would be identical. In fact the two sets are in reasonable agreement, an observation which confirms that the H–H function provides a good fit to the *ab initio*-generated potential functions.

Some of the properties of the B···HF given in Tables 3 and 5 can be compared with those available from experiment. Those members of the B···HF series for which gas-phase experimental investigations have been published are N_2···HF,[6] OC···HF[8,9] and HCN···HF.[11,12] Various of the calculated constants in Tables 3 and 5 have been accurately measured by rotational and high-resolution vibrational spectroscopy and their values are included in Table 5. The agreement between the calculated values and those obtained by experiment is satisfactory, except for α_σ for HCN···HF, which, as was also noted for HCl in the preceding paragraph, is significantly underestimated. It thus appears that *ab initio* calculations at the CCSD(T)(F12c)/cc-pVTZ-F12 explicitly correlated level lead to a reasonably good

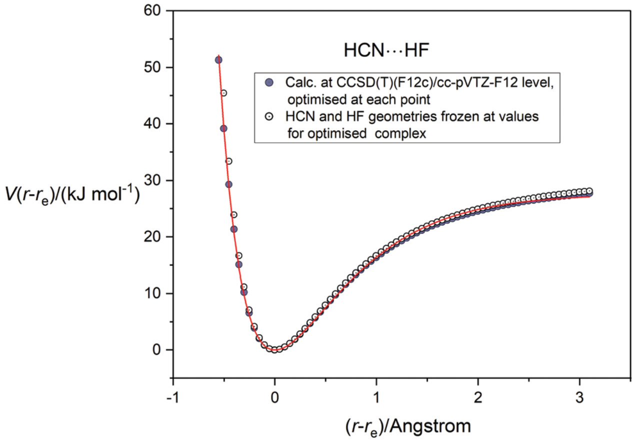

Fig. 7 Comparison of potential energy curve for HCN···HF calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level with geometry relaxation at each point (blue-filled circles) with that calculated at the same level of theory but with the HCN and HF geometries frozen at those appropriate to the equilibrium complex (open circles). The continuous red line is the Hulburt–Hirschfelder function fitted to the relaxed PE points.

representation of the radial potential energy function for the hydrogen-bond stretching mode in those axially symmetric complexes B···HF considered here. Certainly, the H–H function provides a good fit to the *ab initio* curves. If the same percentage errors in the various calculated properties found for HCl were to apply to the B···HF complexes, the agreement would appear better just because the quantities are generally smaller for the complexes.

An alternative approach to fitting the *ab initio*-calculated potential functions of the B···HF complexes by means of the Hulburt–Hirschfelder analytical function is worth investigating. This approach involves holding D_e fixed at its value calculated from the energies E_B, E_{HF} and $E_{B\cdots HF}$ of the B, HF and B···HF geometries optimized at the CCSD(T)(F12c)/cc-pVTZ-F12 level. D_e is related to these energies by the equation

$$D_e = E_{B\cdots HF} - E_B - E_{HF}, \tag{11}$$

Counterpoise correction was applied to correct for BSSE. With D_e so fixed, the remaining three parameters of the H–H function were fitted to the *ab initio* potential curve for each B···HF to give the values of the constants *a*, *b* and *c* recorded in Table 6. These values have larger standard errors than those obtained by fitting all four parameters D_e, *a*, *b*, and *c* (see Table 4), as expected. However, the numerical spectroscopic constants calculated from the them (Table 7) are in good agreement with those shown in Table 5, which were calculated from the H–H constants given in Table 4.

Table 6 Constants of the Hulburt–Hirschfelder analytical potential energy function obtained by fitting the $V(r - r_e)$ *versus* $(r - r_e)$ points generated by calculations at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory. In these fits, D_e was held fixed at the value given by the *ab initio* calculations (see footnote) and *a*, *b* and *c* released

	Hulbert–Hirschfelder function			
Complex	$D_e{}^a$/(kJ mol^{-1})	a/Å^{-1}	b	c
$N_2\cdots HF$	9.46	1.683(11)	0.81(11)	−0.115(7)
$OC\cdots HF$	14.49	1.558(7)	0.873(74)	−0.092(7)
$H_3P\cdots HF$	19.84	1.404(8)	1.01(11)	−0.094(7)
$HCN\cdots HF$	30.70	1.433(22)	0.81(15)	−0.232(16)
$H_3N\cdots HF$	51.61	1.392(10)	3.76(81)	−0.030(8)

[a] Calculated from the CCSD(T)(F12c)/cc-pVTZ-F12 energies of B···HF, B and HF, after counterpoise correction, using the equation $D_e = E_{B\cdots HF} - E_B - E_{HF}$.

3.6 The relationship between D_e and k_σ for the B···HF complexes

Eqn (7) shows the Hulburt–Hirschfelder function requires that $D_e = k_\sigma/2a^2$. Accurate k_σ values are available, given (1) the definition $k_\sigma = V''(r_e)$ (*i.e.* the second derivative of the potential evaluated at the minimum $r = r_e$) and (2) the fact that the region close to the minimum (*i.e.* ±0.1 Å about r_e in steps of 0.025 Å) of

Table 5 Spectroscopic constants associated with the intermolecular stretching mode of the axially symmetric hydrogen-bonded complexes B···HF, where B = N_2, CO, PH_3, HCN and NH_3. The constants were calculated from the parameters of the Hulburt–Hirschfelder potential energy function fitted to the $V(r - r_e)$ *versus* $(r - r_e)$ curve, the latter generated at the CCSD(T)(F12c)/cc-pVTZ-F12 level of theory, in each case

	Spectroscopic property					
Complex	B_e/MHz	D_e/(kJ mol^{-1})	$\omega_\sigma{}^a$/cm^{-1}	$\omega_\sigma x_\sigma{}^a$/cm^{-1}	$\alpha_\sigma{}^a$/MHz	$\nu_\sigma = 1 \leftarrow 0$ wavenumber^a/cm^{-1}
$H^{35}Cl$ (fit to RKR)	317582.622[b]	455.3	2974.5	43.7	8410	2887.0
$H^{35}Cl$ (*ab initio*)	316880.128	455.1	2941.4	38.3	8295	2864.9
$N_2\cdots HF$	3302.814	9.20(1)	114.7	4.91	53.9	104.9
$OC\cdots HF$	3125.996	14.02(2)	131.9	4.07	36.6	123.8
$H_3P\cdots HF$	3550.382	19.02(2)	133.6	3.04	47.3	127.5
$HCN\cdots HF$	3619.792	28.04(5)	180.5	4.29	30.5	171.9
$H_3N\cdots HF$	7437.592	49.21(7)	250.2	3.97	59.5	242.3
Experimental						
$H^{35}Cl$	317582.622[a]	445.39[c]	2990.946[b]	52.8186[b]	9209.1[b]	2885.31
$N_2\cdots HF$	—	8.97[d]	—	—	—	79.5[e]
$OC\cdots HF$	—	15.67[f]	108.7–114.5[g]	3.79	—	107.99(2)[f]
$HCN\cdots HF$	—	26.1(16)[g]	—	—	61.79(3)[h]	197(15)[g], 168.3(2)[i]

[a] The subscript e (rather than σ) is appropriate for $H^{35}Cl$ quantities. [b] Ref. 25. [c] Ref. 17. [d] Ref. 6. D_e is semi-experimental estimate. [e] Ref. 6. [f] Predicted using a high-quality morphed potential function. Ref. 8. [g] Ref. 9. [h] From absolute intensity measurements in the rotational spectrum of HCN···HF. See ref. 11. [i] Ref. 12.

Table 7 Spectroscopic constants associated with the intermolecular stretching mode of the axially symmetric hydrogen-bonded complexes B···HF. The constants were calculated from the parameters *a*, *b* and *c* of Hulburt–Hirschfelder potential energy function fitted to the $V(r - r_e)$ *versus* $(r - r_e)$ curve with D_e fixed at its value calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level (see Table 6)

	Spectroscopic property					
Complex	$B_e{}^a$/MHz	$D_e{}^b$/(kJ mol^{-1})	ω_σ/cm^{-1}	$\omega_\sigma x_\sigma$/cm^{-1}	α_σ/MHz	$\nu_\sigma = 1 \leftarrow 0$ wavenumber/cm^{-1}
$N_2\cdots HF$	3302.814	9.46	113.8	5.12	56.0	103.6
$OC\cdots HF$	3125.996	14.49	130.4	4.23	38.3	121.9
$H_3P\cdots HF$	3550.382	19.84	132.3	3.24	77.3	125.8
$HCN\cdots HF$	3619.792	30.70	175.8	4.70	33.9	166.4
$H_3N\cdots HF$	7437.592	51.61	247.5	4.28	64.2	238.9

[a] Value of equilibrium rotational constant of most abundant isotopologue calculated at CCSD(T)(F12c)/cc-pVTZ-F12 level. [b] Calculated from the CCSD(T)/cc-pVTZ-F12 energies of B···HF, B and HF, after counterpoise correction, using the equation $D_e = E_{B\cdots ClF} - E_B - E_{ClF}$.

Table 8 Two measures (D_e and k_σ) of binding strength for axially-symmetric, hydrogen-bonded complexes B···HF calculated at the CCSD(T)(F12c)/cc-pVTZ-F12 level

Complex	$D_e{}^a$/kJ mol^{-1})	$k_\sigma{}^b$/(N m^{-1})
$N_2\cdots HF$	9.46	9.15
$OC\cdots HF$	14.49	12.11
$H_3P\cdots HF$	19.84	13.36
$HCN\cdots HF$	30.70	22.31
$H_3N\cdots HF$	51.61	34.96

[a] Calculated from the CCSD(T)(F12c)/cc-pVTZ-F12 energies of B···HF, B and HF, after counterpoise correction, using the equation $D_e = E_{B\cdots ClF} - E_B - E_{ClF}$. [b] Calculated from $V''(r_e) = k_\sigma$ by fitting a polynomial around the minimum of the *ab initio*-calculated curves and differentiating.

the CCSD(T)(F12c)/cc-pVTZ-F12 potential function of each B···HF complex can be fitted precisely to a 6th order polynomial (see Section 3.2) and k_σ can then be obtained by differentiation. Moreover, D_e values at this level of theory have been evaluated as the difference between the energies of B···HF and B + HF, [see eqn (11)] after counterpoise correction (which is very small). The two sets of quantities are recorded in Table 8 for the five B···HF complexes investigated. According to eqn (11), if the Hulburt–Hirschfelder function were an exact fit for each of the five B···HF complexes, a plot of D_e *versus* $k_\sigma/(2a^2)$ would be a straight line of gradient 1.000 and intercept 0.000. Fig. 8 shows that such a plot is an excellent straight line, for which the linear regression fit leads to the gradient = 6.17(13) × 10^{23} mol^{-1} or 1.02(2) per molecule, with the intercept 0.005(15) kJ mol^{-1} and R^2 = 0.9986. This result establishes with some accuracy that $D_e = k_\sigma/2a^2$ for the family of the five axially symmetric, hydrogen-bonded complexes B···HF, (B = N_2,CO, PH_3, HCN, NH_3).

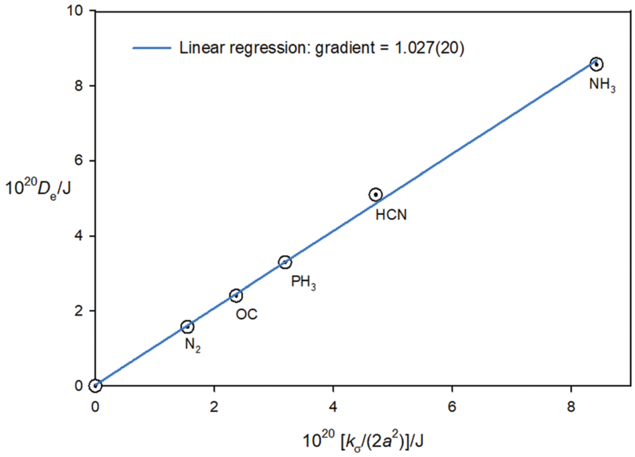

Fig. 8 A plot of the equilibrium dissociation energy D_e *versus* $k_\sigma/(2a^2)$ for five axially-symmetric, hydrogen-bonded complexes B···HF, where B = N_2, CO, PH_3, HCN and NH_3.

4. Conclusions

In this article, several conclusions have been established about the suitability of explicitly correlated *ab initio* calculations at the CCSD(T)(F12c)/cc-pVTZ-F12 level for generating the potential energy changes as a function of the intermolecular distance *r* in the series of axially symmetric, hydrogen-bonded complexes B···HF, when B = N_2, CO, PH_3, HCN and NH_3. The aim was to predict spectroscopic properties of the complexes under the assumption that the component molecules B and HF were sufficiently rigid relative to the intermolecular radial mode ν_σ to allow them to be treated as diatomic molecules in reasonable approximation. Two approaches were followed: (1) eqn (4)–(6) relating the spectroscopic properties ω_σ, $\omega_\sigma x_\sigma$ and α_σ to various derivatives of the potential energy with respect to *r*, evaluated at $r = r_e$ were applied to the *ab initio* generated functions, and (2) the potential function calculated *ab initio* for each B···HF was fitted by Morse, Rydberg and Hulburt–Hirschfelder functions in turn. Analysis of the fits revealed that the four-constant, H–H function provided statistically the best fit in each case. The same sets of spectroscopic properties as considered in (1) were then evaluated from the parameters of the fitted H–H functions. The constants ω_σ, $\omega_\sigma x_\sigma$ and α_σ determined by approaches (1) and (2) were in good agreement, and would be identical if the H–H function were a perfect fit. When compared with the small number of available experimental versions of these constants, the predicted values were in satisfactory agreement with experiment, indicating that potential energy functions calculated in the diatomic approximation for the chosen complexes might provide a guide to the (often demanding) experiments required to measure such quantities.

As a prelude to the discussion of the B···HF, the same procedures were applied to the diatomic molecule H^{35}Cl, for which an accurate RKR-type potential is available. The conclusion for H^{35}Cl was that the CCSD(T)(F12c)/cc-pVTZ-F12 calculations provided an encouragingly good representation of the RKR function and yielded spectroscopic properties in satisfactory (but, of course, not perfect) agreement with the very accurately known experimental values.

It was also established that the relationship $D_e = k_\sigma/(2a^2)$ between the two measures (D_e and k_σ, both calculated *ab initio*) of the strength of the hydrogen bond in the B···HF complexes (and required if the H–H function were an accurate representation of the B···HF potential functions) holds to an excellent level of approximation, and supports the conclusion that the H–H function is appropriate to represent the hydrogen bond in the complexes investigated.

Conflicts of interest

There are no conflicts of interest to report.

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