H₃P···AgI: generation by laser-ablation and characterization by rotational spectroscopy and ab initio calculations†

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The new compound H₃P···AgI has been synthesized in the gas phase by means of the reaction of laser-ablated silver metal with a pulse of gas consisting of a dilute mixture of ICF₃ and PH₃ in argon. Ground-state rotational spectra were detected and assigned for the two isotopologues H₃P···¹⁰⁷AgI and H₃P···¹²⁷AgI in their natural abundance by means of a chirped-pulse, Fourier-transform, microwave spectrometer. Both isotopologues exhibit rotational spectra of the symmetric-top type, analysis of which led to accurate values of the rotational constant B₀, the quartic centrifugal distortion constants D₂ and D₄, and the iodine nuclear quadrupole coupling constant eQq(I) = eQqAg. Ab initio calculations at the explicitly-correlated level of theory CCSD(T)(F12+)/aug-cc-pVDZ confirmed that the atoms P···Ag–I lie on the C₃ axis in that order. The experimental rotational constants were interpreted to give the bond lengths r₀(P···Ag) = 2.3488(20) Å and r₀(Ag–I) = 2.5483(1) Å, in good agreement with the equilibrium lengths of 2.3387 Å and 2.5537 Å, respectively, obtained in the ab initio calculations. Measures of the strength of the interaction of PH₃ and AgI (the dissociation energy D₀ for the process H₃P···AgI = H₃P + AgI and the intermolecular stretching force constant F₀(P···Ag) are presented and are interpreted to show that the order of binding strength is H₃P···HI < H₃P···ICl < H₃P···AgI for these metal-bonded molecules and their halogen-bonded and hydrogen-bonded analogues.

1 Introduction

A programme of systematic investigations of small molecules of the type B···MX is being conducted, where B is a small Lewis base (e.g. N₂, OC, H₂O, H₂S, HC, H₂C=CH₂, cyclopropane or NH₃), M = Cu, Ag or Au, and X = F, Cl or I. The programme has both experimental and theoretical components. The experimental approach is to produce B···MX by laser ablation of the metal M in the presence of a gas pulse composed of small amounts of B and a molecular source of halogen atoms X in a large excess of argon. Following supersonic expansion of the product B···MX entrained in the carrier gas, its rotational spectrum is observed in isolation at a low effective temperature. Various properties of B···MX are available through analysis of the rotational spectrum, namely the angular geometry, the distances r(B···M) and r(M–X), the strength of the intermolecular bond B···M, and the electric charge redistribution that accompanies formation of B···MX. The theoretical component of the investigations involves ab initio calculations at the CCSD(T)(F12+)/aug-cc-pVDZ explicitly correlated level of theory, usually with the largest basis set affordable. These calculations have the advantage of providing accurate properties of the isolated molecule, which can be compared with the experimental results.

Several molecules H₃N···MX, where M = Cu or Ag and X = F, Cl or I, have been detected and characterised recently in the gas phase for the first time through their rotational spectra, although H₃N···CuCl was identified in the solid state earlier. Each was established to be a symmetric-top molecule, with the N···MX nuclei lying on the top (C₃v) axis, in the order indicated. To date, analogues of H₃N···MX having phosphine instead of ammonia as the Lewis base B have not been identified experimentally, to the best of our knowledge, but several have been the subject of density functional calculations. We report here the rotational spectrum of H₃P···Ag–I and some of its properties derived therefrom.

There is some evidence that molecules B···MX (M = Cu, Ag, or Au; X = F, Cl, or I) have geometries that are isomorphic...
with those of their hydrogen-bonded \((B \cdots \cdot XH, X \text{ is a halogen atom})^{23}\) and halogen-bonded \((B \cdots \cdot XY, XY \text{ is a dihalogen molecule})^{24}\) counterparts, but are more strongly bound and exhibit a greater electric charge rearrangement within the diatomic subunit. Our interest here is to examine the geometry and binding strength of \(H_3P \cdots \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot
spectroscopic constants were the rotational constant \( B_0 \), the quartic centrifugal distortion constants \( D_J \) and \( D_K \), and the iodine nuclear quadrupole coupling constant \( \chi_{\text{quad}} = -eQe^{2}V/\alpha a^{2} = eQg_{\text{quad}} \) (where \( q_{\text{quad}} \) is the electric field gradient along the \( C_3^* \) axis direction). The magnetic coupling of the iodine nuclear spin to the molecular rotation can in principle be described by the spin-rotation constant \( C_{ab} \) but this constant was too small to be determined from the observed frequencies. Values of the spectroscopic constants from the final cycle of the least-squares fit with PGOPHER are given in Table 1 for the two isotopologues \( \text{H}_3\text{P} \cdots 107\text{AgI} \) and \( \text{H}_3\text{P} \cdots 109\text{AgI} \) investigated, together with \( \sigma_{\text{RMS}} \), the RMS deviation of the fit, and \( N^* \), the number of hyperfine components fitted. Spectra simulated using PGOPHER and the final set of spectroscopic constants are shown in Fig. 1. The detailed PGOPHER fits are available as Supplementary Material. The values of \( \sigma_{\text{RMS}} \) are satisfactory, given the estimated accuracy of frequency measurement (12 kHz) associated with the chirped-pulse F-T microwave spectrometer.

### 3.2 Molecular geometry

The facts that the ground-state rotational spectrum of the detected complex of phosphine and argentous iodide is of the symmetric-top type and that the Ag atom is close to the complex centre of mass (see later) mean that the arrangement of the atoms is either \( \text{H}_3\text{P} \cdots \text{AgI} \) or \( \text{PH}_3 \cdots \text{AgI} \). The second of these is unlikely because \( ^{109}\text{I} \cdots ^{109}\text{AgI} \) is dipolar in the indicated sense and it is expected that the positive end of the electric dipole would interact with the P non-bonding electron pair, which lies on the \( C_3 \) axis of phosphine. This expectation is confirmed by \textit{ab initio} calculations at the CCSD(T)(F12*)/AVDZ level of theory, which predict that the optimised geometry of \( \text{PH}_3 \cdots \text{AgI} \) lies higher in energy by 116 kJ mol\(^{-1} \) than that of the \( \text{H}_3\text{P} \cdots \text{AgI} \) conformer. The higher energy conformer would not be populated at the low effective temperature (\( \sim 2 \) K) of the supersonic expansion. The observed conformer is therefore of the general form shown in Fig. 2.

The rotational constants \( B_0 = C_0 \) for the two isotopologues \( \text{H}_3^{31}\text{P} \cdots 107\text{AgI} \) and \( \text{H}_3^{33}\text{P} \cdots 109\text{AgI} \) allow only a partial determination of the lengths of the H–P, P–Ag and Ag–I bonds and of the angle \( \alpha = \angle \text{HPAg} \) (between the P–H bond and the \( C_3 \) axis) necessary to define the \( r_0 \) geometry. The quantities of most interest are \( r_0(P \cdots Ag) \) and \( r_0(Ag \cdots I) \). The \textit{ab initio} calculations indicate that \( r_0(P \cdots H) \) decreases by 0.0114 Å when phosphine enters the complex and the angle \( \zeta \) decreases by 3.94°. We shall assume that the \( r_0 \) geometry of phosphine \( [r_0(P \cdots H) = 1.420003 \text{ Å}] \) and angle \( \zeta_0 = 122.86° \) obtained by fitting the accurately known \(^5\text{B}_0 \) and \( C_0 \) using the STRFIT program of Kisiel \(^{43} \) changes in the same way as does the \( r_0 \) geometry on formation of \( \text{H}_3\text{P} \cdots \text{AgI} \). If so, \( r_0(P \cdots H) = 1.4086 \text{ Å} \) and \( \zeta_0 = 118.92° \) are appropriate to \( \text{PH}_3 \) in the complex. When these values were assumed in a fit of the ground-state principal moments of inertia of \( \text{H}_3^{31}\text{P} \cdots 107\text{AgI} \) and \( \text{H}_3^{31}\text{P} \cdots 109\text{AgI} \), the values \( r_0(P \cdots Ag) = 2.3488 \text{ Å} \) and \( r_0(Ag \cdots I) = 2.5483 \text{ Å} \) resulted. No errors in these quantities are generated in the fit because two constants are fitted by two parameters. However, calculations reveal the following variations: \( \delta r(P \cdots Ag) \delta r(P \cdots H) = 0.065, \delta r(Ag \cdots I) \delta r(P \cdots H) = 0.005, \delta r(P \cdots Ag) \delta \zeta = 0.002 \text{ Å deg}^{-1} \), and \( \delta r(Ag \cdots I) \delta \zeta = 0.0001 \text{ Å deg}^{-1} \). Thus, the length \( r_0(Ag \cdots I) \) is very insensitive to changes to the geometry of \( \text{PH}_3 \) that might occur when \( \text{H}_3\text{P} \cdots \text{AgI} \) is formed. These partial derivatives lead, when the reasonable errors of \( \delta r_0 = 0.005 \text{ Å} \) and \( \delta \zeta_0 = 1° \) are assumed, to \( r_0(P \cdots Ag) = 2.3488(20) \text{ Å} \) and \( r_0(Ag \cdots I) = 2.5483(1) \text{ Å} \). The results from the CCSD(T)(F12*)/AVDZ optimisation of \( \text{H}_3\text{P} \cdots \text{AgI} \) are 2.3387 Å and 2.5537 Å, respectively.

The fact that spectroscopic constants have been determined for the isotopologues \( \text{H}_3\text{P} \cdots 107\text{AgI} \) and \( \text{H}_3\text{P} \cdots 109\text{AgI} \) allows the coordinate \( \alpha_{\text{Ag}} \) to be obtained by the substitution method from the expression

\[
\alpha_{\text{Ag}}^2 = \Delta \nu_0^{2}/h_{\text{ms}}
\]

in which \( \Delta \nu_0^{2} \) is the difference in the zero-point moments of inertia of the two isotopologues and \( M_{\text{mass}} = \frac{M \Delta \text{mass}}{M + \Delta \text{mass}} \), where \( M \) is the mass of the parent and \( \Delta \text{mass} \) is the mass change accompanying the isotopic substitution at Ag. The result is \( |\alpha_{\text{Ag}}| = 0.9017(17) \text{ Å} \), where the error is estimated from \( \delta r_{0} = 0.0015/|\alpha| \) as recommended by Costain.\(^{46} \) The corresponding values for this coordinate implied by the determined \( r_0 \) geometry and the \textit{ab initio} \( r_0 \) geometry are 0.9017 Å and 0.9056 Å, respectively.

### 3.3 Strength of the interaction of \( \text{H}_3\text{P} \) and AgI

There are two common measures of the strength of the interaction of phosphine and silver iodide in \( \text{H}_3\text{P} \cdots \text{AgI} \). Both are properties of the one-dimensional potential-energy function associated with variation of the distance \( r(P \cdots Ag) \) when \( C_3 \) symmetry is maintained but with structural relaxation at each point (referred to as the dissociation coordinate). The first is the intermolecular stretching quadratic force constant \( F_{P \cdots Ag} \).
The second is the energy, $D_{e1}$, required to dissociate $H_3P\cdots AgI$ to give $PH_3$ and $AgI$ at infinite separation, with reactants and products at their equilibrium geometries. The first can be obtained from the experimental centrifugal distortion constants $D_2$ but the second is not available from the present experiments. Both are available from the $ab initio$ calculations.

For weakly bound complexes (such as most hydrogen-bonded complexes $B\cdots HX$, where $B$ is a simple Lewis base and $X$ is a halogen atom) it is a good approximation to assume that $B$ and $HX$ are rigid and unchanged in geometry on complex formation. Then $F_{B\cdots HX}$ can be related to the equilibrium centrifugal distortion constant $D_{J}'$ or $D_{J}''$ (depending on molecular symmetry) of the complex and the various rotational constants of $B$, $HX$ and $B\cdots HX$, as demonstrated by Novick for the case where $B$ is an atom and with Millen for a wider range of molecules $B$. For complexes $B\cdots MX$, where $M$ is a coinage metal atom, the intermolecular bond can be strong and the approximation that the force constant $F_{B\cdots MX}$ is much smaller than all other stretching force constants is no longer appropriate. To deal with such cases, we have recently described a two-force constant model which relates the quadratic force constants $F_{MX}$ and $F_{B\cdots MX}$ (hereafter referred to as $F_{11}$ and $F_{22}$, respectively) to either $D_{J}'$ or $D_{J}''$ under the assumption that the contribution of the cross term $F_{12}$ is negligible. The model applies to all complexes of a Lewis base $B$ with any diatomic molecule (e.g. a hydrogen halide $HX$, a dihalogen $XY$, or a coinage metal halide $MX$) as long as the diatomic molecule lies along a symmetry axis of $B$ in the equilibrium geometry. Note that $B$ is assumed rigid, but can be changed in geometry when subsumed into the complex. During the vibrational motion no further change is assumed, however.

The two-force constant model for a symmetric-top molecule such as $H_3P\cdots AgI$ leads (with numbering of the $Ag$ and $I$ atoms and internal coordinates $r_1$ and $r_2$ shown in Fig. 2) to the expression

$$hD_{J}' = \frac{1}{2} \left( \frac{\hbar^2}{I_{bb}} \right)^{1/4} \left\{ (m_1a_1)^2 (F^{(1)}_{11}) + (m_1a_1 + m_2a_2)^2 (F^{(1)}_{22}) \right\}$$

In eqn (3), $I_{bb}$ is an equilibrium principal moment of inertia and the $a_n$ are equilibrium principal axis coordinates of atoms $n = 1$ and 2. The compliance matrix elements $\{F^{(1)} - I_{nn}\}$ are simply $1/I_{mm}$ under the approximations described above. It was shown in ref. 50 that zero-point constants and coordinates can be used in place of equilibrium values to a reasonable approximation. Least-squares fitting of $(F^{(1)}_{11})$ and $(F^{(1)}_{22})$ simultaneously to the $D_{J}'$ values of the two isotopologues $H_3P\cdots 107AgI$ and $H_3P\cdots 109AgI$ led to ill-conditioning, however, so instead a fixed value of $F_{11}$ was assumed and $F_{22}$ was fitted. Fig. 3 shows $F_{22}$ plotted as a function of $F_{11}$ for a wide range of values of the latter, with the equilibrium value of the force constant 145.8 N m$^{-1}$ of the free diatomic molecule $AgI$ indicated, as calculated from its equilibrium vibrational wavenumber. If it is assumed that $F_{11}$ is unchanged from the equilibrium value in $AgI$ of 145.8 N m$^{-1}$, the result is $F_{22} = 122(5)$ N m$^{-1}$, where the error is that transmitted from the fit of the $D_{J}'$ values.

It is also possible to calculate $F_{11}$ and $F_{22} ab initio$. At the CCSD(T)(F12*)/AVDZ level of theory the results are $F_{11} = 151.1$ N m$^{-1}$ and $F_{22} = 106.8$ N m$^{-1}$. When the $D_{J}'$ values are fitted by using eqn (3) with $F_{11}$ fixed at 151.1 N m$^{-1}$, the result is $F_{22} = 110(5)$ N m$^{-1}$, where the error is that implied by the error in the $D_{J}'$ values, and is the best present experimental estimate for this quantity. For free $AgI$ at the same level of theory, $F_{11} = 145.9$ N m$^{-1}$ is obtained, in excellent agreement with the experimental equilibrium value of 145.8 N m$^{-1}$. Thus, $F_{11}$ increases by 3.5% when $AgI$ is incorporated into $H_3P\cdots AgI$. For comparison, the lower level of theory MP2/aug-cc-pVTZ-PP gives $F_{11} = 168.8$ N m$^{-1}$ and $F_{22} = 130.1$ N m$^{-1}$ when using the GAUSSIAN package.

The result for free $AgI$ at the same level is $F_{11} = 160.1$ N m$^{-1}$, corresponding to 9.8% overestimation of the experimental equilibrium value. If $F_{11}$ for $H_3P\cdots AgI$ were also overestimated by a similar percentage, the corrected value would be $F_{11} = 153$ N m$^{-1}$, which likewise represents a small increase relative to that of the free molecule.

It has been shown that in the limit of rigid, unchanged $B$ and $MX$ geometries, when $F_{11}$ becomes infinite, eqn (3) reduces to the corresponding Millen expression

$$D_{J}' = 16\pi^2 \mu B_{MX} \left( 1 - \frac{B_{B\cdots MX}}{B_{B\cdots MX}} \right) \left( \frac{F^{(1)}_{11}}{F^{(1)}_{22}} \right)^2$$

in which $B_{B\cdots MX}$, $B_{B\cdots MX}$ and $B_{MX}$ are equilibrium rotational constants of the complex and its components, but zero-point values are used of necessity. In eqn (4), $\mu = m_B m_{MX}/(m_B + m_{MX})$.

When $B = H_3P$ and $MX = AgI$, a fit of the centrifugal distortion constants $D_{J}'$ of the isotopologues $H_3P\cdots 107AgI$ and $H_3P\cdots 109AgI$ using zero-point rotational constants given in Tables 1 and 2 leads to $F_{22} = 31.3(3)$ N m$^{-1}$, which is a very serious underestimate. The reason why becomes clear when the plot of $F_{22}$ as a function of $F_{11}$ is extended to cover a wider range of $F_{11}$ values and unphysical solutions for which $F_{22}$ is negative are included. The result is the rectangular hyperbola shown in Fig. 4. The...
horizontal asymptote \((F_i = \infty)\) gives \(F_{22} = 31.26\) N m\(^{-1}\) and corresponds to the solution when AgI is rigid and unperturbed when within \(\text{H}_3\text{P} \cdot \cdot \cdot \text{AgI}\). The vertical asymptote \((108.39\) N m\(^{-1}\)) corresponds to the lowest possible value of \(F_{11}\) consistent with the observed \(D_j^0\). Clearly, any reasonable \(F_{11}\) must lead to a \(F_{22}\) value that is considerably greater than that given by eqn (4).

The other measure of the strength of binding is the dissociation energy defined earlier; it takes the value \(D_e = 116\) kJ mol\(^{-1}\) when calculated at the CCSD(T)(F12*)/AVDZ level of theory, after counterpoise correction.\(^{52}\) The value for AgI = Ag + I at the same level of theory is 230 kJ mol\(^{-1}\). It is therefore clear from the \(D_e\) value and the force constant \(F_{22}\) that the intermolecular bond in \(\text{H}_3\text{P} \cdot \cdot \cdot \text{AgI}\) is by no means weak. In fact by either measure, the P – Ag bond is about an order of magnitude stronger than most hydrogen or halogen bonds, but is only about a factor of two weaker than the Ag–I bond itself.

### 3.4 Electric charge redistribution on formation of \(\text{H}_3\text{P} \cdot \cdot \cdot \text{AgI}\)

The iodine nuclear quadrupole coupling constant \(\lambda_{\text{AgI}}(I) = eq_I^\text{AgI}Q_I^\text{AgI}\) carries information about the electric charge distribution at I through the electric field gradient \(q_I^\text{AgI}\) along the \(a\)-axis direction at the iodine nucleus. According to the Townes–Dailey model\(^{13}\) for interpreting such coupling constants, the ionicity \(i_c\) (or fractional ionic character) of the free AgI molecule is given by

\[
i_c = 1 + \frac{\lambda_{\text{AgI}}(I)}{eq_I^\text{AgI}Q_I^\text{AgI}},
\]

in which \(q_I^\text{AgI}(1,0,0)\) is the contribution to the electric field gradient at I along the \(a\)-axis direction that arises from an electron in 5p orbital. The quantity \(eq_I^\text{AgI}(1,0,0)\) has the value 2292.71 MHz when described as a frequency.\(^{54}\) Eqn (5) leads to the result \(i_c = 0.537\) for \(^{107}\text{Ag}^{27}\text{I}\) (the values\(^{51,55}\) of several properties of AgI, including \(\lambda_{\text{AgI}}(I)\), are collected in Table 2) but has the value 0.680 for the complex \(\text{H}_3\text{P} \cdot \cdot \cdot ^{107}\text{Ag}^{27}\text{I}\). Evidently, the charge rearrangement within AgI on formation of the complex is significant, a result consistent with the similar magnitude of the values for the dissociation energies \(D_e\) for the processes \(\text{H}_3\text{P} \cdot \cdot \cdot \text{AgI} = \text{H}_3\text{P} + \text{AgI}\) and \(\text{AgI} = \text{Ag} + \text{I}\) referred to earlier. Interestingly, there appears to be very little change in its bond length when AgI is subsumed into the complex.

### 4 Conclusions

The new molecule \(\text{H}_3\text{P} \cdot \cdot \cdot \text{AgI}\) has been synthesized in the gas phase by a laser ablation method in which a pulse of gas mixture consisting of a few per cent each of PH3 and ICF3, with the remainder Ar, interacts with the plasma produced when silver is ablated by a Nd-YAG laser operating at 532 nm. The product was detected and characterised by means of its rotational spectrum, as observed with a chirped-pulse, Fourier-transform microwave spectrometer. The molecule is a symmetric top of \(C_{3v}\) symmetry with the atoms P, Ag and I lying in that order on the symmetry axis \(a\). Spectroscopic constants determined by fitting the observed transitions of the isotopologues \(\text{H}_3\text{P} \cdot \cdot \cdot ^{107}\text{AgI}\) and \(\text{H}_3\text{P} \cdot \cdot \cdot ^{109}\text{AgI}\) were interpreted to give the values \(r_0(\text{P} \cdot \cdot \cdot \text{Ag}) = 2.3488(20)\) Å and \(r_0(\text{Ag} \cdot \cdot \cdot \text{I}) = 2.5483(1)\) Å for the indicated bond lengths, after assuming changes to the \(r_0\) geometry of free PH3 when bound up in the complex were the same as the corresponding changes in the \(r_e\) geometry, as predicted \textit{ab initio} at the CCSD(T)(F12*)/AVDZ level of theory. It is of interest to note that the value of \(r_0(\text{Ag} \cdot \cdot \cdot \text{I})\) is increased by only 0.0017 Å relative to the free AgI value of 2.5466 Å (see Table 2).\(^{55}\) Interpretation of the centrifugal distortion constants \(D_j^0\) and the iodine nuclear quadrupole coupling constants led to a value \(F_{22} = 110\) (5) N m\(^{-1}\) for the quadratic stretching force constant of the P – Ag bond and to a value \(\Delta \delta_c = 0.14\) for the increase in the Ag–I bond ionicity when \(\text{H}_3\text{P} \cdot \cdot \cdot \text{AgI}\) is formed. Although the ionicity of AgI increases significantly when subsumed into the complex, we note that the

### Table 2: Some properties of \(\text{H}_3\text{P}\) and \(\text{AgI}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>(\text{H}_3\text{P})</th>
<th>Property</th>
<th>(107\text{AgI})</th>
<th>(109\text{AgI})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_0/\text{MHz})</td>
<td>133480.1165(17)</td>
<td>(B_0/\text{MHz})</td>
<td>1342.99237(7)</td>
<td>1329.61831(7)</td>
</tr>
<tr>
<td>(C_0/\text{MHz})</td>
<td>11749.4357(77)</td>
<td>(\lambda_{\text{AgI}}(I)/\text{MHz})</td>
<td>-1062.3229(13)</td>
<td>-1062.5280(14)</td>
</tr>
<tr>
<td>(r_0(\text{P} \cdot \cdot \cdot \text{Ag})/\text{Å})</td>
<td>1.42000(6)</td>
<td>(r_0(\text{Ag} \cdot \cdot \cdot \text{I})/\text{Å})</td>
<td>2.546627</td>
<td>2.546617</td>
</tr>
<tr>
<td>(I_{(\text{HPH})}/\text{MHz})</td>
<td>93.345(6)</td>
<td>(F_{22}/(\text{N m}^{-1}))</td>
<td>145.76(3)</td>
<td>145.76(3)</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. 44.\(^{b}\) Ref. 35.\(^{c}\) Calculated by fitting the zero-point rotational constants using the program STRFIT (ref. 45).\(^{d}\) Calculated from the equilibrium vibrational wavenumber \(\nu_0\) given in ref. 51 by using the expression \(F_{\text{AgI}} = 4\pi^2\nu_0^2\mu_{\text{AgI}},\) where \(\mu_{\text{AgI}} = m_{\text{Ag}}m_{\text{I}}/(m_{\text{Ag}} + m_{\text{I}})\).
length of the bond and its force constant $F_{11}$ are effectively unchanged.

H$_3$N$\cdot$CuI, synthesized and characterised recently by a similar method, is isomorphic with H$_3$P$\cdot$AgI and has $r_e(N\cdot Cu)=1.9357(13)$ Å and $r_d(Cu-I)=2.3553(5)$ Å, the latter representing an increase of only 0.0147 Å relative to the free Cu–I value of 2.34059 Å. The N···Cu interaction strength, as measured by $F_{22}=110(30)$ N m$^{-1}$, is similar to that at 110(5) N m$^{-1}$ of P$\cdot$Ag in H$_3$P$\cdot$AgI, but the ab initio value for the other measure of binding strength for H$_3$N$\cdot$CuI ($D_p=168$ kJ mol$^{-1}$) is significantly larger than that (116 kJ mol$^{-1}$) of H$_3$P$\cdot$AgI. The increase, $\delta_k=0.14$, in the ionicity of the Cu–I bond when H$_3$N$\cdot$CuI is formed is identical to that observed for H$_3$P$\cdot$AgI. We conclude that H$_3$P$\cdot$AgI and H$_3$N$\cdot$CuI are very similar in their properties: both are strongly bound, both have similar changes in the ionicity of the I–M bond when the free MI molecule is subsumed into the complex, but the bond length $r_d(M-I)$ is effectively unchanged in both by this process.

Several complexes involving hydrogen bonds and halogen bonds to ammonia and phosphine have been described elsewhere, namely H$_3$P$\cdot$HI,$^{25}$ H$_3$N$\cdot$HI,$^{36}$ H$_3$P$\cdot$ICl$^{27}$ and H$_3$N$\cdot$ICl$^{28}$ All have $C_{3v}$ symmetry, with all atoms but the three H atoms of PH$_3$ or NH$_3$ lying on the $C_3$ axis and therefore all are isomorphous with H$_3$P$\cdot$AgI. The hydrogen-bonded analogues H$_3$P$\cdot$HI and H$_3$N$\cdot$HI have also been discussed in a detailed review,$^{36}$ where it is concluded, based on several indirect observations, that there is little evidence of significant charge rearrangement or HI bond lengthening in these two complexes. Both are weakly bound, having quadratic force constants $F_{22}=F_{F_{11}}$ or $F_{N_{11}}$ of 3.4 N m$^{-1}$ and 7.2 N m$^{-1}$, respectively. These values are more than an order of magnitude smaller than those of H$_3$P$\cdot$AgI and H$_3$N$\cdot$Cu when $F_{P}\cdot Ag$ or $F_{N}\cdot Cu$ are calculated from the centrifugal distortion constant $D_J$ by means of eqn (3), the more accurate method for strongly bound complexes. The related halogen-bonded H$_3$P$\cdot$ICl$^{27}$ and H$_3$N$\cdot$ICl$^{28}$ have $F_{22}=F_{F_{11}}=20.8$ N m$^{-1}$ and $F_{22}=F_{F_{11}}=30.4$ N m$^{-1}$, respectively, when obtained by means of eqn (4). As indicated earlier, the larger is $F_{22}$ relative to $F_{11}$, the more serious will be its underestimation when eqn (4) is used. This underestimation is likely to be negligible for H$_3$P$\cdot$HI and H$_3$N$\cdot$HI, but it is possible that the values of $F_{22}$ for H$_3$P$\cdot$ICl and H$_3$N$\cdot$ICl will both be somewhat larger (but only by a few %) than those reported previously. Clearly, the halogen-bonded complexes H$_3$P$\cdot$ICl and H$_3$N$\cdot$ICl are significantly more strongly bound than the hydrogen-bonded species H$_3$P$\cdot$HI and H$_3$N$\cdot$HI (when using the $F_{22}$ criterion) but less so than H$_3$P$\cdot$AgI and H$_3$N$\cdot$Cu. According to a method of estimating electric charge redistribution from the changes in the I and Cl nuclear quadrupole coupling constants,$^{27,28,57}$ there is a net movement of 0.15e (where e = electronic charge) from Cl to I in ICl when each of H$_3$P$\cdot$ICl and H$_3$N$\cdot$ICl is formed, thereby suggesting similar charge movement to that observed in each of H$_3$P$\cdot$AgI and H$_3$N$\cdot$Cu.

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