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$H_3P\cdots AgI$: generation by laser-ablation and characterization by rotational spectroscopy and *ab initio* calculations†

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The new compound $H_3P\cdots AgI$ 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 ICF_3 and PH_3 in argon. Ground-state rotational spectra were detected and assigned for the two isotopologues $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$ 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 B_0, the quartic centrifugal distortion constants D_J and D_{JK}, and the iodine nuclear quadrupole coupling constant $\chi_{aa}(\mathrm{I}) = eQq_{aa}$. *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 C_3 axis in that order. The experimental rotational constants were interpreted to give the bond lengths $r_0(\mathrm{P\cdots Ag}) = 2.3488(20)$ Å and $r_0(\mathrm{Ag{-}I}) = 2.5483(1)$ 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 PH_3 and AgI (the dissociation energy D_e for the process $H_3P\cdots AgI = H_3P + AgI$ and the intermolecular stretching force constant $F_{\mathrm{P\cdots Ag}}$) are presented and are interpreted to show that the order of binding strength is $H_3P\cdots HI < H_3P\cdots ICl < H_3P\cdots AgI$ 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.* N_2, OC, H_2O, H_2S, HC≡CH, $H_2C{=}CH_2$, cyclopropane or NH_3), M = Cu, Ag or Au, and X = F, Cl or I.[1–19] 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*) 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 $H_3N\cdots MX$, 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,[17–19] although $H_3N\cdots CuCl$ was identified in the solid state earlier.[20] Each was established to be a symmetric-top molecule, with the N···MX nuclei lying on the top (C_3) axis, in the order indicated. To date, analogues of $H_3N\cdots MX$ 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.[21,22] We report here the rotational spectrum of $H_3P\cdots Ag{-}I$ 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)[1–19] have geometries that are isomorphic

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with those of their hydrogen-bonded (B$\cdots$HX, X is a halogen atom)[23] and halogen-bonded (B$\cdots$XY, XY 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 $H_3P\cdots Ag–I$ and the electric charge redistribution within Ag–I that accompanies its formation. These properties will then be compared with those of the closely related molecule $H_3N\cdots CuI$,[19] with those of their hydrogen-bonded analogues $H_3P\cdots HI$[25] and $H_3N\cdots HI$[26] and with those of their halogen-bonded relatives, $H_3P\cdots ICl$[27] and $H_3N\cdots ICl$.[28]

2 Experimental and theoretical methods

2.1 Detection of the rotational spectrum

A chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer fitted with a laser ablation source was used to observe rotational spectra in the frequency range 6.5 to 18.5 GHz. Detailed descriptions of the spectrometer and laser ablation source are available elsewhere.[29,30] A gas sample containing ∼4.0% PH_3 and ∼1.5% CF_3I in argon was prepared at a total pressure of 6 bar. The sample was pulsed over the surface of a silver rod that was ablated by a suitably timed Nd:YAG laser pulse (wavelength 532 nm, pulse duration 10 ns, pulse energy 20 mJ). Subsequently, the gas pulse expanded supersonically into the vacuum chamber of the spectrometer. The rod was translated and rotated regularly at small intervals to allow each laser pulse (repetition rate of ∼1.05 Hz) to impinge on a fresh metal surface and thereby ensure shot-to-shot reproducibility.

The sequence employed to record broadband microwave spectra involves repetition of two steps. The first is polarization of the sample by a microwave chirp that sweeps from 6.5 to 18.5 GHz within 1 μs and the second is recording of the subsequent free induction decay of the molecular emission over a 20 μs time period. This sequence is repeated eight times during the expansion of each gas sample pulse into the spectrometer chamber. The free induction decay (FID) of the polarization is mixed down with the signal from a 19 GHz local oscillator and then digitized by means of a 25 Gs s^{-1} digital oscilloscope. Each transition is observed as a single peak with full-width at half-maximum (fwhm) ≅ 150 kHz after application of a Kaiser–Bessel digital filter.

2.2 *Ab initio* calculations

Structure optimizations and counter-poise corrected dissociation energies were calculated using the Turbomole package[31] at the CCSD(T)(F12*) level of theory,[32] a coupled-cluster method with single and double excitations, explicit correlation,[33] and a perturbative treatment of triple excitations.[34] Only valence electrons were included in the correlation treatment. A basis set combination consisting of aug-cc-pVDZ on H and P atoms and aug-cc-pVDZ-PP on Ag and I atoms was used and will be referred to by AVDZ. ECP-10-MDF[35,36] and ECP-28-MDF[37] were used on Ag and I, respectively, to account for scalar relativistic effects. For the density fitting approximation used to accelerate the CCSD(T)(F12*) calculation, the respective def2-QZVPP basis sets were employed for the MP2[38,39] and Fock[40] terms. For the complementary auxiliary basis required for the F12 treatment,[41] the aug-cc-pCVDZ MP2 density fitting basis sets were used.[39] Quadratic force constants were also calculated at this level of theory. For comparison, the same force constants were calculated with the GAUSSIAN 09 package[42] at the MP2 level of theory. A basis set combination consisting of aug-cc-pVTZ on the H and P atoms, and aug-cc-pVTZ-PP on the Ag and I atoms was used in this case.

3 Results

3.1 Determination of spectroscopic constants

The observed spectrum of $H_3P\cdots AgI$ showed evidence of the presence of the two isotopologues $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$, each exhibiting iodine nuclear quadrupole hyperfine structure, as may be seen from consideration of Fig. 1. An iterative least-squares fit of the observed hyperfine frequencies of each isotopologue was conducted using the program PGOPHER, written and maintained by Western.[43] The Hamiltonian employed was of the form

$$H = H_{\mathrm{R}} - \frac{1}{6}\mathbf{Q}{:}\nabla\mathbf{E}, \tag{1}$$

where H_{R} is the usual energy operator appropriate to a semi-rigid symmetric rotor molecule and $-\frac{1}{6}\mathbf{Q}{:}\nabla\mathbf{E}$ is the iodine nuclear quadrupole energy operator, in which $\mathbf{Q}$ is the iodine nuclear electric quadrupole moment tensor and $\nabla\mathbf{E}$ is the electric field gradient tensor at I. The matrix of H was constructed in the coupled symmetric-rotor basis $\boldsymbol{I} + \boldsymbol{J} = \boldsymbol{F}$. The only determinable

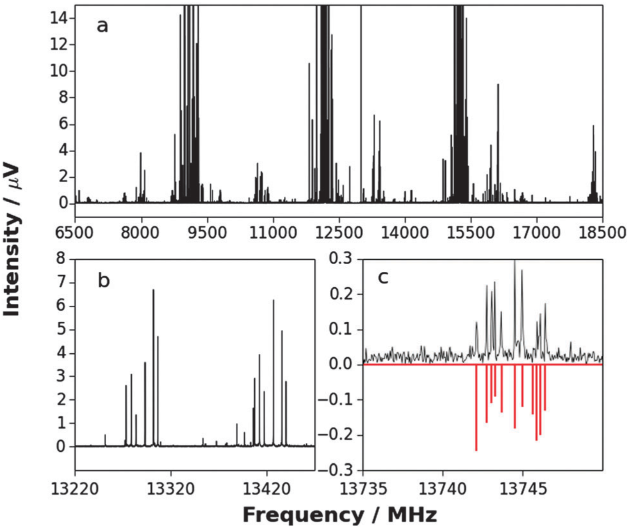

Fig. 1 Top panel: (a) broadband spectrum recorded while probing a sample containing CF_3I, Ag and PH_3 (530k FIDs). Some transitions of CF_3I are taken off-scale to allow weaker transitions to be distinguished from the baseline. (b) Expanded section of spectrum displayed in (a) to show $J' - J'' = 5–4$ transitions of ^{107}AgI (∼13 420 MHz) and ^{109}AgI (∼13 280 MHz). Hyperfine splittings in each transition are evident. (c) Expanded section of the spectrum displayed in (a) to show $J' - J'' = 11–10$ transition of $H_3P\cdots{}^{109}AgI$ (black). A simulated spectrum that uses the results of fitted parameters is displayed inverted (red).

Table 1 Observed spectroscopic constants[a] of $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$

Spectroscopic constant	$H_3P\cdots{}^{107}AgI$	$H_3P\cdots{}^{109}AgI$
B_0/MHz	626.01307(23)	624.76423(17)
D_J/kHz	0.03182(89)	0.03238(64)
D_{JK}/kHz	4.46(14)	4.04(10)
χ_{aa}(I)/MHz	−733.83(34)	−734.54(27)
σ_{RMS}[b]/kHz	12.0	9.0
N[c]	88	93

[a] Numbers in parentheses are one standard deviation in units of the last significant digits. [b] Standard deviation of the fit. [c] Number of hyperfine frequencies included in the fit.

spectroscopic constants were the rotational constant B_0, the quartic centrifugal distortion constants D_J and D_{JK}, and the iodine nuclear quadrupole coupling constant $\chi_{aa}(I) = -eQ\partial^2V/\partial a^2 = eQq_{aa}$ (where $q_{aa} = -\partial^2V/\partial a^2$ is the electric field gradient along the C_3^a 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_{bb} but this constant was too small to determine 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 $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$ investigated, together with σ_{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 σ_{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 $H_3P\cdots AgI$ or $PH_3\cdots AgI$. The second of these is unlikely because $^{\delta+}Ag–I^{\delta-}$ 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 *ab initio* calculations at the CCSD(T)(F12*)/AVDZ level of theory, which predict that the optimised geometry of $PH_3\cdots AgI$ lies higher in energy by 116 kJ mol^{-1} than that of the $H_3P\cdots AgI$ conformer. The higher energy conformer would not be populated at the low effective temperature (∼2 K) of the supersonic expansion. The observed conformer is therefore of the general form shown in Fig. 2.

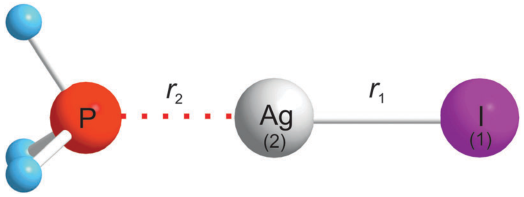

Fig. 2 The molecular geometry of $H_3P\cdots AgI$ drawn to scale. The internal coordinates r_1 and r_2 used in the discussion of how to obtain force constant F_{22} from the centrifugal distortion constants D_J^0 are indicated. The experimental zero-point values of r_1 and r_2 are r_0(Ag–I) = 2.5483(1) Å and $r_0(P\cdots Ag)$ = 2.3488(20) Å, respectively.

The rotational constants $B_0 = C_0$ for the two isotopologues $H_3{}^{31}P\cdots{}^{107}Ag^{127}I$ and $H_3{}^{31}P\cdots{}^{109}Ag^{127}I$ allow only a partial determination of the lengths of the H–P, P⋯Ag and Ag–I bonds and of the angle $\alpha = \angle HPAg$ (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–I). The *ab initio* calculations indicate that r_e(P–H) decreases by 0.0114 Å when phosphine enters the complex and the angle α_e decreases by 3.94°. We shall assume that the r_0 geometry of phosphine (r_0(P–H) = 1.420003 Å and angle α_0 = 122.86° obtained by fitting the accurately known[44] B_0 and C_0 using the STRFIT program of Kisiel[45]) changes in the same way as does the r_e geometry on formation of $H_3P\cdots Ag–I$. If so, r_0(P–H) = 1.4086 Å and α_0 = 118.92° are appropriate to PH_3 in the complex. When these values were assumed in a fit of the ground-state principal moments of inertia of $H_3{}^{31}P\cdots{}^{107}Ag^{127}I$ and $H_3{}^{31}P\cdots{}^{109}Ag^{127}I$, the values $r_0(P\cdots Ag)$ = 2.3488 Å and r_0(Ag–I) = 2.5483 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: $\partial r(P\cdots Ag)/\partial r(P–H) = 0.065$, $\partial r(Ag–I)/\partial r(P–H) = 0.005$, $\partial r(P\cdots Ag)/\partial\alpha = 0.002$ Å deg^{-1}. and $\partial r(Ag–I)/\partial\alpha = 0.0001$ Å deg^{-1}. Thus, the length r_0(Ag–I) is very insensitive to changes to the geometry of PH_3 that might occur when $H_3P\cdots AgI$ is formed. These partial derivatives lead, when the reasonable errors of δr_0 = 0.005 Å and $\delta\alpha_0$ = 1° are assumed, to $r_0(P\cdots Ag)$ = 2.3488(20) Å and r_0(Ag–I) = 2.5483(1) Å. The results from the CCSD(T)(F12*)/AVDZ optimisation of $H_3P\cdots AgI$ are 2.3387 Å and 2.5537 Å, respectively.

The fact that spectroscopic constants have been determined for the isotopologues $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$ allows the coordinate a_{Ag} to be obtained by the substitution method from the expression

$$a_{Ag}{}^2 = \Delta I_b^0/\mu_s, \tag{2}$$

in which ΔI_b^0 is the difference in the zero-point moments of inertia of the two isotopologues and $\mu_s = \dfrac{M\Delta m}{M + \Delta m}$, where M is the mass of the parent and Δm is the mass change accompanying the isotopic substitution at Ag. The result is $|a_{Ag}|$ = 0.9017(17) Å, where the error is estimated from $\delta a = 0.0015/|a|$ as recommended by Costain.[46,47] The corresponding values for this coordinate implied by the determined r_0 geometry and the *ab initio* r_e geometry are 0.9017 Å and 0.9056 Å, respectively.

3.3 Strength of the interaction of H_3P and AgI

There are two common measures of the strength of the interaction of phosphine and silver iodide in $H_3P\cdots AgI$. Both are properties of the one-dimensional potential-energy function associated with variation of the distance $r(P\cdots Ag)$ when C_{3v} 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_e, 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_J 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 $F_{B\cdots H}$ can be related to the equilibrium centrifugal distortion constant D_J^e or $\varDelta_J^e$ (depending on molecular symmetry) of the complex and the various rotational constants of B, HX and $B\cdots HX$, as demonstrated by Novick[48] for the case where B is an atom and by Millen[49] 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 $F_{B\cdots M}$ 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 $F_{M\text{–}X}$ and $F_{B\cdots M}$ (hereafter referred to as F_{11} and F_{22}, respectively) to either D_J^e or $\varDelta_J^e$ under the assumption that the contribution of the cross term F_{12} is negligible.[50] 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 C_n ($n \geq 2$) 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[50]

$$hD_J^e = \frac{1}{2}\left\{\frac{\hbar^4}{\left(I_{bb}^e\right)^4}\right\}\left\{(m_1a_1)^2\left(F^{-1}\right)_{11} + (m_1a_1 + m_2a_2)^2\left(F^{-1}\right)_{22}\right\} \tag{3}$$

In eqn (3), I_{bb}^e 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 $(F^{-1})_{nn}$ are simply $1/F_{nn}$ 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^0 values of the two isotopologues $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$ 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 Ag–I indicated, as calculated from its equilibrium vibrational wavenumber.[51] If it is assumed that F_{11} is unchanged from the equilibrium value in free 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^0 values.

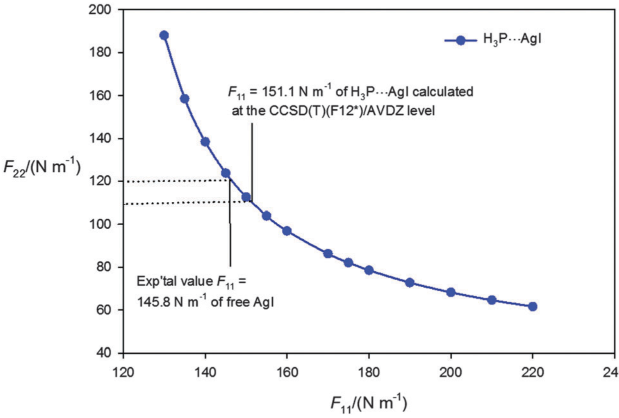

Fig. 3 Values of the quadratic intermolecular stretching force constant F_{22} obtained by fitting the centrifugal distortion constants D_J^0 of the isotopologues $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$ using eqn (3) at fixed values of the AgI stretching force constant F_{11} in the range 130 to 220 N m^{-1}. Eqn (3) is valid only if the off-diagonal force constant F_{12} is assumed to be zero. The CCSD(T)(F12*)/AVDZ-F12 value of F_{11}, the experimental equilibrium value for the free AgI molecule and the F_{22} values they correspond to are indicated.

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^0 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^0 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.[42] 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[49]

$$D_J = 16\pi^2\mu B_D{}^3\left(1 - \frac{B_{B\cdots MX}}{B_B} - \frac{B_{B\cdots MX}}{B_{MX}}\right)\left(F^{-1}\right)_{22}, \tag{4}$$

in which $B_{B\cdots MX}$, B_B 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^0 of $H_3P\cdots{}^{107}AgI$ and H_3P ${}^{109}AgI$ (using zero-point rotational constants given in Tables 1 and 2) leads to F_{22} = 31.3(5) 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

Table 2 Some properties of H_3P and Ag–I

Property	H_3P^a	Property	$^{107}AgI^b$	$^{109}AgI^b$
B_0/MHz	133480.1165(17)	B_0/MHz	1342.99237(7)	1329.61831(7)
C_0/MHz	117489.4357(77)	χ_{aa}(I)/MHz	−1062.5299(15)	−1062.5230(14)
r_0(P–H)/Å	1.42000^c	r_0(Ag–I)/Å	2.546627	2.546617
∠(HPH)/°	93.345^c	F_{AgI}/(N m^{-1})	145.78(3)^d	145.76(3)^d

[a] Ref. 44. [b] Ref. 55. [c] Calculated by fitting the zero-point rotational constants using the program STRFIT (ref. 45). [d] Calculated from the equilibrium vibrational wavenumber ω_e given in ref. 51 by using the expression $F_{AgI} = 4\pi^2\omega_e{}^2c^2\mu_{AgI}$, where $\mu_{AgI} = m_{Ag}m_I/(m_{Ag} + m_I)$.

horizontal asymptote ($F_{11} = \infty$) gives F_{22} = 31.26 N m^{-1} and corresponds to the solution when AgI is rigid and unperturbed when within $H_3P\cdots AgI$. 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 $H_3P\cdots AgI$ 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 $H_3P\cdots AgI$

The iodine nuclear quadrupole coupling constant $\chi_{aa}(I) = eq_{aa}^{I}Q^{I}$ carries information about the electric charge distribution at I through the electric field gradient q_{aa}^{I} along the *a*-axis direction at the iodine nucleus. According to the Townes–Dailey model[53] for interpreting such coupling constants, the ionicity i_c (or fractional ionic character) of the free AgI molecule is given by

$$i_c = 1 + \frac{\chi_{aa}(I)}{eQ^{I}q^{I}_{(5,1,0)}}, \tag{5}$$

in which $q^{I}_{(5,1,0)}$ is the contribution to the electric field gradient at I along the *a*-axis direction that arises from an electron in $5p_a$ orbital. The quantity $eQ^{I}q^{I}_{(5,1,0)}$ has the value 2292.71 MHz when described as a frequency.[54] Eqn (5) leads to the result i_c = 0.537 for $^{107}Ag^{127}I$ (the values[51,55] of several properties of AgI, including χ_{aa}(I), are collected in Table 2) but has the value 0.680 for the complex $H_3P\cdots{}^{107}Ag^{127}I$. 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 $H_3P\cdots AgI = H_3P + AgI$ and AgI = Ag + I referred to earlier. Interestingly, there appears to be very little change in its bond length when AgI is subsumed into the complex.

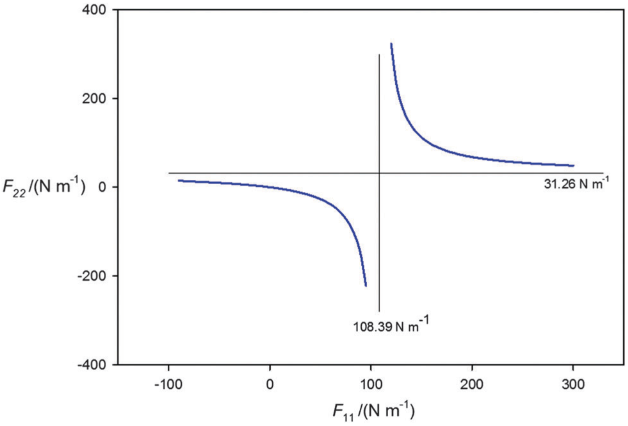

Fig. 4 The rectangular hyperbola obtained by following the procedure described in the caption to Fig. 3, but with the range of assumed F_{11} values extended from −100 to +300 N m^{-1}. The negative values of F_{22} and F_{11} are unphysical. The asymptote at F_{11} = 108.39 N m^{-1} represents the value of that force constant below which a negative, unphysical value of F_{22} is required to fit the centrifugal distortion constants D_J^0. The asymptote at F_{22} = 31.26 N m^{-1} is the value of this force constant in the limit $F_{11} = \infty$ N m^{-1}, that is when the MX molecule is rigid. It can be shown[50] that if both PH_3 and AgI were rigid and unperturbed on formation of $H_3P\cdots AgI$ eqn (3) leads to the Millen eqn (4), when equilibrium spectroscopic constants are used in the latter.

4 Conclusions

The new molecule $H_3P\cdots Ag{-}I$ 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 PH_3 and ICF_3, 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 $H_3P\cdots{}^{107}AgI$ and $H_3P\cdots{}^{109}AgI$ were interpreted to give the values r_0(P⋯Ag) = 2.3488(20) Å and r_0(Ag–I) = 2.5483(1) Å for the indicated bond lengths, after assuming changes to the r_0 geometry of free PH_3 when bound up in the complex were the same as the corresponding changes in the r_e geometry, as predicted *ab initio* at the CCSD(T)(F12*)/AVDZ level of theory. It is of interest to note that the value of r_0(Ag–I) is increased by only 0.0017 Å relative to the free AgI value of 2.54663 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 δi_c = 0.14 for the increase in the Ag–I bond ionicity when $H_3P\cdots AgI$ is formed. Although the ionicity of AgI increases significantly when subsumed into the complex, we note that the length of the bond and its force constant F_{11} are effectively unchanged.

$H_3N\cdots CuI$, synthesized and characterised recently by a similar method,[19] is isomorphic with $H_3P\cdots AgI$ and has $r_0(N\cdots Cu)$ = 1.9357(13) Å and r_0(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 110(5) N m^{-1} of P···Ag in $H_3P\cdots AgI$, but the *ab initio* value for the other measure of binding strength for $H_3N\cdots CuI$ (D_e = 168 kJ mol^{-1}) is significantly larger than that (116 kJ mol^{-1}) of $H_3P\cdots AgI$. The increase, δi_c = 0.14, in the ionicity of the Cu–I bond when $H_3N\cdots CuI$ is formed is identical to that observed for $H_3P\cdots AgI$. We conclude that $H_3P\cdots AgI$ and $H_3N\cdots CuI$ are very similar in their properties: both are strongly bound, both have similar changes in the ionicity of the M–I bond when the free MI molecule is subsumed into the complex, but the bond length r_0(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 $H_3P\cdots HI$,[25] $H_3N\cdots HI$,[26] $H_3P\cdots ICl$[27] and $H_3N\cdots ICl$.[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^a axis and therefore all are isomorphic with $H_3P\cdots AgI$. The hydrogen-bonded analogues $H_3P\cdots HI$ and $H_3N\cdots HI$ have also been discussed in a detailed review,[56] 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} = $F_{P\cdots H}$ or $F_{N\cdots H}$ 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 $H_3P\cdots AgI$ and $H_3N\cdots CuI$ when $F_{P\cdots Ag}$ or $F_{N\cdots Cu}$ are calculated from the centrifugal distortion constant D_J^0 by means of eqn (3), the more accurate method for strongly bound complexes. The related halogen-bonded $H_3P\cdots ICl$[27] and $H_3N\cdots ICl$[28] have $F_{22} = F_{P\cdots I}$ = 20.8 N m^{-1} and F_{22} = $F_{P\cdots I}$ 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 $H_3P\cdots HI$ and $H_3N\cdots HI$, but it is possible that the values of F_{22} for $H_3P\cdots ICl$ and $H_3N\cdots ICl$ will both be somewhat larger (but only by a few %) than those reported previously. Clearly, the halogen-bonded complexes $H_3P\cdots ICl$ and $H_3N\cdots ICl$ are significantly more strongly bound than the hydrogen-bonded species $H_3P\cdots HI$ and $H_3N\cdots HI$ (when using the F_{22} criterion) but less so than $H_3P\cdots AgI$ and $H_3N\cdots CuI$. 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 0.15*e* (where *e* = electronic charge) from Cl to I in ICl when each of $H_3P\cdots ICl$ and $H_3N\cdots ICl$ is formed, thereby suggesting similar charge movement to that observed in each of $H_3P\cdots AgI$ and $H_3N\cdots CuI$.

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