12-2017

Molecular Geometries and Other Properties of H\(_2\)O⋯AgI and H\(_3\)N⋯AgI as Characterised by Rotational Spectroscopy and ab initio Calculations

Chris Medcraft

Eva Gougoula

Dror M. Bittner

Old Dominion University

John C. Mullaney

Susana Blanco

See next page for additional authors

Follow this and additional works at: https://digitalcommons.odu.edu/chemistry_fac_pubs

Part of the Biochemistry Commons, and the Chemistry Commons

Repository Citation

Medcraft, Chris; Gougoula, Eva; Bittner, Dror M.; Mullaney, John C.; Blanco, Susana; Tew, David P.; Walker, Nicholas R.; and Legon, Anthony C., "Molecular Geometries and Other Properties of H\(_2\)O⋯AgI and H\(_3\)N⋯AgI as Characterised by Rotational Spectroscopy and ab initio Calculations" (2017). Chemistry & Biochemistry Faculty Publications. 98.

https://digitalcommons.odu.edu/chemistry_fac_pubs/98

Original Publication Citation

Molecular geometries and other properties of $\text{H}_2\text{O}\#\text{AgI}$ and $\text{H}_3\text{N}\#\text{AgI}$ as characterised by rotational spectroscopy and ab initio calculations

Chris Medcraft, Eva Gougoula, Dror M. Bittner, John C. Mullaney, Susana Blanco, David P. Tew, Nicholas R. Walker, and Anthony C. Legon

Citation: The Journal of Chemical Physics 147, 234308 (2017); View online: https://doi.org/10.1063/1.5008744
View Table of Contents: http://aip.scitation.org/toc/jcp/147/23
Published by the American Institute of Physics

Articles you may be interested in

Structure, spectroscopy, and dynamics of the phenol-(water)$_2$ cluster at low and high temperatures
The Journal of Chemical Physics 147, 234307 (2017); 10.1063/1.5006055

Halogen bonding properties of 4-iodopyrazole and 4-bromopyrazole explored by rotational spectroscopy and ab initio calculations
The Journal of Chemical Physics 147, 214303 (2017); 10.1063/1.5002662

Towards a quantum chemical protocol for the prediction of rovibrational spectroscopic data for transition metal molecules: Exploration of CuCN, CuOH, and CuCCH
The Journal of Chemical Physics 147, 234303 (2017); 10.1063/1.5006931

Channel branching ratios in $\text{CH}_2\text{CN}^-$ photodetachment: Rotational structure and vibrational energy redistribution in autodetachment
The Journal of Chemical Physics 147, 234309 (2017); 10.1063/1.5001475

The reactivity of the Criegee intermediate $\text{CH}_3\text{CHOO}$ with water probed by FTMW spectroscopy
The Journal of Chemical Physics 148, 014308 (2018); 10.1063/1.5009033

Photodissociation of van der Waals complexes of iodine X–I$_2$ ($X = \text{I}_2, \text{C}_2\text{H}_4$) via charge-transfer state: A velocity map imaging investigation
The Journal of Chemical Physics 147, 234304 (2017); 10.1063/1.5001104
Molecular geometries and other properties of H$_2$O···AgI and H$_3$N···AgI as characterised by rotational spectroscopy and ab initio calculations

Chris Medcraft,1 Eva Gougoula,1 Dror M. Bittner,2 John C. Mullaney,1 Susana Blanco,3 David P. Tew,4 Nicholas R. Walker,1,a) and Anthony C. Legon4,a)

1Chemistry-School of Natural and Environmental Sciences, Newcastle University, Bedson Building, Newcastle-upon-Tyne NE1 7RU, United Kingdom
2Department of Chemistry and Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, Virginia 23529-0126, USA
3Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain
4School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, United Kingdom

(Received 9 October 2017; accepted 27 November 2017; published online 20 December 2017)

The rotational spectra of H$_3$N···AgI and H$_2$O···AgI have been recorded between 6.5 and 18.5 GHz by chirped-pulse Fourier-transform microwave spectroscopy. The complexes were generated through laser vapourisation of a solid target of silver or silver iodide in the presence of an argon gas pulse containing a low concentration of the Lewis base. The gaseous sample subsequently undergoes super-sonic expansion which results in cooling of rotational and vibrational motions such that weakly bound complexes can form within the expanding gas jet. Spectroscopic parameters have been determined for eight isotopologues of H$_3$N···AgI and six isotopologues of H$_2$O···AgI. Rotational constants, $B_0$; centrifugal distortion constants, $D_J$, $D_{JK}$ or $A_J$, $A_{JK}$; and the nuclear quadrupole coupling constants, $\chi_{aa}(I) = \chi_{bb}(I) = \chi_{cc}(I)$ are reported. H$_3$N···AgI is shown to adopt a geometry with a $C_3v$ symmetry. The geometry of H$_2$O···AgI is $C_5$ at equilibrium but with a low barrier to inversion such that the vibrational wavefunction for the $\nu = 0$ state has $C_{2v}$ symmetry. Trends in the nuclear quadrupole coupling constant of the iodine nucleus, $\chi_{aa}(I)$, of L···AgI complexes are examined, where L is varied across the series (L = Ar, H$_3$N, H$_2$O, H$_2$S, H$_2$P, or CO). The results of experiments are reported alongside those of ab initio calculations at the CCSD(T)(F12*)/AVXZ level ($X = T, Q$). Published by AIP Publishing. https://doi.org/10.1063/1.5008744

I. INTRODUCTION

Microwave spectroscopy has recently been applied to explore the molecular structures of complexes in which a Lewis base is attached to either CuX, AgX, or AuX (where X is a halogen atom) to form L···MX,1–11 where, for example, L = H$_2$O,1,10 H$_2$S, 3–5 NH$_3$,12 C$_2$H$_6$,6,8,11 or CO.13,14 The same technique has also been applied to study complexes that are similar in composition and structure but distinct in that L is not a typical Lewis base. For example, H$_2$···MX,15,16 Ar···MX,17–19 Kr···MX,18,20 and Xe···MX21 have each been characterised. Significant structural changes were identified in each of H$_2$S,15,16 C$_2$H$_6$,6,8,11 and C$_2$H$_4$0 in their attachment to a coinage metal atom. Both H$_2$O···MX and H$_2$S···MX adopt pyramidal geometries of $C_5$ symmetry at equilibrium. H$_2$O···MX complexes were observed to undergo rapid inversion between two equivalent $C_5$ geometries on the time scale of a molecular rotation such that the geometry of H$_2$O···MX is effectively $C_{2v}$ (planar) in the $\nu = 0$ state.3–5,10,22 Rotational spectroscopy has proven to be a powerful tool for investigation of the structure and dynamics in such complexes. Previous studies have made comparisons with hydrogen- and halogen-bonded complexes of similar geometrical structure.

Examination of the trend in the nuclear quadrupole coupling constant of chlorine, $\chi_{aa}$(Cl), across the L···AgCl series revealed that the attachment of Ar to AgCl19 induces only a very small change in the quantity relative to the value of the parameter in diatomic AgCl. The described change varies with L in the order CO > H$_2$S > H$_3$N > H$_2$O. A very similar trend was observed in the equivalent L···CuCl series.4,6,10,12,17 The variation in $\chi_{aa}$(Cl) provides an indication of the extent of electron redistribution accompanying the formation of each of these complexes. Evidently, stabilisation of OC···MCI through back-donation of electrons from d orbitals of the metal onto $\pi^*$ orbitals of CO leads to a stronger interaction than that existing within Ar···MCI. The present work aims to determine rotational constants, centrifugal distortion constants, and nuclear quadrupole coupling constants of the L···AgI complexes for which L = H$_2$O or H$_3$N and use these quantities to draw conclusions about the geometries, interaction strength, and electric charge redistribution associated with the complexes. The results will...
be compared with those from recent studies of other L···AgI to allow trends to be established across a wide range of L···AgI for the first time.

II. METHODS

A. Experimental

Broadband microwave spectra were measured using a chirped-pulse Fourier-transform microwave (CP-FTMW) spectrometer fitted with a laser ablation source. Detailed descriptions of the spectrometer and laser ablation source are provided in Refs. 9 and 23. The method employed to generate H$_2$N···AgI is identical to that used previously during a study of H$_2$S···AgI. A gas sample containing a low concentration of precursors is diluted in argon and prepared at a total pressure of 6 bars. The sample is prepared to contain ~1.5% CF$_3$I and ~4.0% NH$_3$. The mixed sample is introduced into the spectrometer via a pulsed nozzle where it passes over the surface of a silver rod from which material is ablated by the 2nd harmonic of an Nd:YAG laser pulse ($\lambda = 532$ nm, pulse duration of 10 ns, pulse energy of 20 mJ). The rotational and vibrational motions of molecules are subsequently cooled through supersonic expansion of the gas sample. The target rod is continually translated and rotated to expose a fresh surface to each laser pulse and ensure shot-to-shot reproducibility of signal intensities. Pulses are introduced with a repetition rate of approximately 2 Hz. Observations of rotational transition intensities suggest that the rotational temperature of probed species is of the order of 2 K. The generation of H$_2$O···AgI was achieved while using a solid target rod composed of silver iodide combined with a bespoke sample holder containing water and placed immediately in front of the nozzle. Attempts to generate H$_2$O···AgI through vaporisation of a silver rod in the presence of gaseous H$_2$O and CF$_3$I precursors were unsuccessful. Isotopically enriched samples of $^{15}$NH$_3$ (Sigma-Aldrich, 98% $^{15}$N), ND$_3$ (Sigma-Aldrich, 99% D), D$_2$O, and H$_2^{18}$O were used to generate and record the spectra of isotopologues as appropriate.

The sequence employed to record broadband microwave spectra involves (i) polarization of the sample by a microwave chirp that sweeps from 6.5 to 18.5 GHz within 1 $\mu$s and then (ii) recording of the free induction decay (FID) of the molecular emission over a period of 20 $\mu$s. The sequence of (i) and (ii) is repeated eight times following each gas sample introduction pulse. The free induction decay (FID) of the polarization is digitized at 25 GS/s using a digital oscilloscope after down-mixing against a 19 GHz local oscillator. Frequency-domain spectra are obtained through Fourier transformation of the time-domain data to give a full width at half maximum (FWHM) of 100 kHz. The spectra of H$_3$N···AgI and H$_2$O···AgI were averaged for 600 k and 570 k free induction decays (FIDs), respectively, prior to being Fourier transformed.

B. Ab initio calculations

Geometry optimisations and frequency calculations were performed using the MOLPRO$^{25}$ and TURBOMOLE$^{26}$ packages at the CCSD(T)(F12*)$^{27}$ level of theory. The latter is a coupled-cluster method that includes single and double excitations, explicit correlation,$^{28}$ and a perturbative treatment of triple excitations.$^{29}$ Basis set combinations consisting of aug-cc-pVXZ (X = T, Q) on C, H, and N and aug-cc-pVXZ-PP (X = T, Q) on Ag and I with relativistic effective core potentials MDF-28$^{30,31}$ were used and will be referred to as AVXZ (X = T, Q). For the density fitting approximation which was used to accelerate the CCSD(T)(F12*) calculation, the respective def2-QZVPP basis sets were employed for the MP2 and Fock$^{32}$ terms. For the complementary auxiliary basis required for the F12 treatment,$^{33}$ the def2-TZVPP MP2 density fitting basis sets$^{32}$ were used. Only valence electrons were included in the correlation treatment.

III. RESULTS

A. Measurement of transition frequencies

1. H$_3$N···AgI

As described in Sec. II A, the generation of H$_3$N···AgI was achieved by using CF$_3$I and NH$_3$ diluted in argon carrier gas interacting with the plasma produced by ablating silver. Transitions of CF$_3$I molecules were observed with high intensity, as were those of AgI. Transitions of CF$_3$I···NH$_3$ were also observed but more weakly. Spectra containing AgI are distinctive by virtue of the characteristic isotopic abundance ratio of the two isotopes of silver and the hyperfine splitting introduced by the iodine nucleus ($I = 5/2$). This distinctiveness greatly assisted the initial assignments of the spectra of H$_3$N···AgI as shown in Fig. 1. Subsequent experiments employed synthetically enriched isotopic samples to confirm that these complexes are the carriers of the observed spectra and allowed measurements of shifts in the frequencies of transitions following isotopic substitution(s).

Spectra of the partially deuterated complexes, HD$_2$N···AgI, were recorded in addition to that of D$_2$N···AgI during experiments that employed ND$_3$. It is assumed that HD$_2$N was generated through reaction of a fraction of the introduced ND$_3$ sample with H$_2$O or NH$_3$ (perhaps present as a contaminant) within the sample vessel.

![FIG. 1. Expanded section of the spectrum recorded in the 6.5-18.5 GHz frequency range for H$_3$N···$^{105}$AgI (left) and H$_3$N···$^{107}$AgI (right) showing the $(J+1) \leftarrow J = 10 \leftarrow 9$ transition. Blue and red downward pointing lines indicate the simulated spectra of isotopologues containing $^{109}$Ag and $^{107}$Ag, respectively.](image-url)
2. $\text{H}_2\text{O} \cdots \text{AgI}$

Laser vaporisation of silver iodide in the presence of argon and a low concentration of $\text{H}_2\text{O}$ allowed the observation of intense features that assign to the AgI diatomic molecule. Transitions of the Ar···AgI complex characterised previously and a distinctive transition of the water dimer near $12,321 \text{ MHz}$ were also observed. Series of other transitions share some qualitative features of the spectrum of Ar···AgI but were clearly associated with a different molecular carrier. The frequency increment between $(J + 1) \leftarrow J$ transitions was consistent with a lighter molecule than Ar···AgI suggesting H$_2$O···AgI as a possible carrier (Fig. 2). Subsequent experiments to probe HDO···AgI and H$_2^{18}$O···AgI isotopologues revealed isotopic shifts consistent with the assignment to H$_2$O···AgI.

B. Spectroscopic analysis

Parameters of the Hamiltonian shown in Eq. (1) were fitted to measured transition frequencies using Western’s program PGOPER for each molecule,

$$H = H_R - \frac{1}{6} \mathbf{Q}(I) \cdot \nabla \mathbf{E}(I),$$

(1)

where $H_R$ is Watson’s A-reduced Hamiltonian in the $\Gamma$ representation for a semi-rigid symmetric top in the case of H$_2$N···AgI. For such symmetric-top species, ground-state rotational constants are denoted by $A_0$, $B_0$, and $C_0$ and the determinable quartic centrifugal distortion constants are denoted by $D_J$ and $D_{JK}$ which appear in $H_R$. Fits of the transition frequencies of H$_2$O···AgI, and also of the D$_2$HN···AgI isotopologue of H$_3$N···AgI, employed the version of $H_R$ appropriate to a semi-rigid, nearly prolate asymmetric top. The only centrifugal distortion constants of H$_2$O···AgI that contributed significantly to transition frequencies reported here were $\Delta_J$ and $\Delta_{JK}$.

The second term of Eq. (1) describes coupling of the electric quadrupole moment of the I nucleus with the electric field gradient at that nucleus, where $\mathbf{Q}(I)$ is the iodine nuclear quadrupole moment dyadic and $\nabla \mathbf{E}(I)$ is the dyadic of the electric field gradient at the iodine nucleus. The nuclear quadrupole coupling constants of iodine are denoted by $\chi_{aa}(I)$ and $\chi_{bb}(I)$, and the latter required only when fitting the spectra of H$_2$O···AgI. It was unnecessary to include the corresponding term that describes nuclear quadrupole coupling associated with $^{14}$N ($I = 1$) in the Hamiltonian of Eq. (1) because hyperfine structure arising from this nucleus was not apparent in the observed spectra of H$_3$N···AgI at the resolution of the present experiments. The naturally occurring isotopes of silver, $^{107}$Ag and $^{109}$Ag, each have $I = \frac{1}{2}$ and consequently nuclear electric quadrupole moments of zero. Magnetic nuclear spin-rotation and spin-spin interactions were not observed at the resolution of the present experiments, consistent with previous observations performed on similar molecules. A Kaiser-Bessel window function was used to perform the Fourier transform of data for both H$_3$N···AgI and H$_2$O···AgI.

The spectroscopic constants evaluated for the various isotopologues of H$_3$N···AgI and H$_2$O···AgI are provided

| TABLE I. Experimentally determined spectroscopic constants of isotopologues of H$_3$N···AgI. |
|-----------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| $\text{H}_2\text{N} \cdots ^{107}\text{AgI}$ | $\text{H}_2\text{N} \cdots ^{109}\text{AgI}$ | $\text{D}_2\text{N} \cdots ^{107}\text{AgI}$ | $\text{D}_2\text{N} \cdots ^{109}\text{AgI}$ |
| $B_0$ (MHz) | 866.07(45) | 862.33(78) | 808.39(51) | 805.38(72) |
| $D_J$ (kHz) | 0.08(33) | 0.08(44) | 0.06(22) | 0.06(32) |
| $D_{JK}$ (kHz) | 8.6(30) | 8.4(27) | 7.0(24) | 6.9(15) |
| $\chi_{aa}(I)$ (MHz) | -79.5(45) | -79.5(31) | -79.4(61) | -79.4(76) |
| $N^b$ | 18 | 24 | 19 | 19 |
| $\sigma_{r.m.s.}^c$ (kHz) | 9.9 | 11.3 | 10.0 | 6.9 |

$^a$Numbers in parentheses are the standard deviation in units of the last significant figure.

$^b$Number of nuclear quadrupole hyperfine components included in the fit.

$^c$Root mean square deviation of the fit.
TABLE II. Experimentally determined spectroscopic constants of isotopologues of H$_3$N$\cdots$AgI containing $^{15}$N or D.

<table>
<thead>
<tr>
<th></th>
<th>H$_3^{15}$N$\cdots$AgI</th>
<th>H$_3^{15}$N$\cdots$AgI</th>
<th>HD$_2$N$\cdots$AgI</th>
<th>HD$_2$N$\cdots$AgI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(B_0 + C_0)/2$ (MHz)</td>
<td>850.20711(23)$^{a,b}$</td>
<td>846.68067(30)$^b$</td>
<td>1653.18868(38)</td>
<td>1646.7204(34)</td>
</tr>
<tr>
<td>$D_J$ (kHz)</td>
<td>0.0645(12)</td>
<td>0.0662(14)</td>
<td>0.0628$^c$</td>
<td>0.0611(75)$^e$</td>
</tr>
<tr>
<td>$D_{JK}$ (kHz)</td>
<td>8.62(13)</td>
<td>8.55(17)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>$\chi_{av}(I)$ (MHz)</td>
<td>$-796.90(26)$</td>
<td>$-796.66(31)$</td>
<td>$-794.3(19)$</td>
<td>$-795.9(30)$</td>
</tr>
<tr>
<td>$N^a$</td>
<td>41</td>
<td>28</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>$\sigma_{rms,^b}$ (kHz)</td>
<td>7.3</td>
<td>8.1</td>
<td>9.7</td>
<td>14.0</td>
</tr>
</tbody>
</table>

*aNumbers in parentheses are the standard deviation in units of the last significant figure.

*bResults for H$_3^{15}$N$\cdots$AgI and H$_3^{15}$N$\cdots$AgI are included in this table for concise presentation. Note that $B_0 = C_0 = (B_0 + C_0)/2$ for this symmetric rotor.

*cWatson’s $A$ reduction was employed.

*dNumber of nuclear quadrupole hyperfine components included in the fit.

*eRoot mean square deviation of the fit.

TABLE III. Experimentally determined spectroscopic constants of isotopologues of H$_2$O$\cdots$AgI.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O$\cdots$AgI</th>
<th>H$_2$O$\cdots$AgI</th>
<th>H$_2^{18}$O$\cdots$AgI</th>
<th>H$_2^{18}$O$\cdots$AgI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(B_0 + C_0)$ (MHz)</td>
<td>1690.1972(28)$^b$</td>
<td>1683.2961(28)</td>
<td>1629.6036(72)</td>
<td>1623.4861(13)</td>
</tr>
<tr>
<td>$(B_0 + C_0)$ (MHz)</td>
<td>1.64674(20)</td>
<td>1.63346(20)</td>
<td>1.52831(40)</td>
<td>1.51669(46)</td>
</tr>
<tr>
<td>$\Delta_J$ (kHz)</td>
<td>0.07072(79)</td>
<td>0.07111(77)</td>
<td>0.0649(17)</td>
<td>0.0593(28)</td>
</tr>
<tr>
<td>$\Delta_{JK}$ (kHz)</td>
<td>8.642(91)</td>
<td>8.628(87)</td>
<td>8.80(17)</td>
<td>8.69(19)</td>
</tr>
<tr>
<td>$\chi_{av}(I)$ (MHz)</td>
<td>$-885.54(11)$</td>
<td>$-885.33(10)$</td>
<td>$-884.24(49)$</td>
<td>$-885.10(71)$</td>
</tr>
<tr>
<td>$(\chi_{bb}(I) - \chi_{cc}(I))$ (MHz)</td>
<td>$-12.73(28)$</td>
<td>$-12.79(25)$</td>
<td>$-13.6(13)$</td>
<td>$-13.2(17)$</td>
</tr>
<tr>
<td>$N^b$</td>
<td>75</td>
<td>68</td>
<td>40</td>
<td>27</td>
</tr>
<tr>
<td>$\sigma_{rms,^b}$ (kHz)</td>
<td>5.5</td>
<td>5.1</td>
<td>9.6</td>
<td>9.3</td>
</tr>
</tbody>
</table>

*aNumbers in parentheses are the standard deviation in units of the last significant figures.

*bNumber of nuclear quadrupole hyperfine components included in the fit.

*eRoot mean square deviation of the fit.

in Tables I–IV. Only R-branch, $a$-type transitions$^{39}$ having $K_{-1} = 0$ or 1 were observed for H$_3^{14}$N$\cdots$AgI, H$_3^{14}$N$\cdots$AgI, and H$_2^{16}$O$\cdots$AgI, as expected for molecules having a large rotational constant $A_0$, which ensures rotational energy levels having $K_{-1} \geq 2$ are too high in energy to be detectably populated at the temperature of the expanded gas pulse. The rotational constant, $A_0$, could not be determined from the available data for either the symmetric-top species, H$_3^{15}$N$\cdots$AgI, or for the nearly prolate asymmetric rotor, H$_2^{18}$O$\cdots$AgI. This parameter was therefore fixed equal to the appropriate calculated values 180 GHz and 60 GHz, when fitting data and simulating spectra for H$_3$N$\cdots$AgI and H$_2$O$\cdots$AgI, respectively. For H$_2$O$\cdots$AgI and H$_2^{18}$O$\cdots$AgI, transitions having $K_{-1} = 0$ or 1 were observed, which allowed determination of $(B_0 + C_0)$ and $(B_0 + C_0)$. Transitions having $K_{-1} = 1$ were not observed for HD$_2$N$\cdots$AgI or HDO$\cdots$AgI so $B_0 - C_0$ was fixed to zero when fitting $K_{-1} = 0$ transitions for these species. All other isotopologues for which data were recorded are symmetric rotors. The output files of spectroscopic fits performed in PGOPHER are provided as the supplementary material.

For the H$_2$O$\cdots$AgI, HDO$\cdots$AgI, and H$_2^{18}$O$\cdots$AgI isotopologues, rotational transitions of the type $(J + 1) \leftarrow J$ were observed and were regularly separated in energy by a factor of $B_0 + C_0$. As indicated, determination of the $B_0 - C_0$ value for H$_2$O$\cdots$AgI and H$_2^{18}$O$\cdots$AgI was possible due to the detection of $K_{-1} = 1$ transitions. For HDO$\cdots$AgI, only $K_{-1} = 0$ transitions were observed. The ratio of relative intensities of the $K_{-1} = 1$ and $K_{-1} = 0$ transitions (for a given $(J + 1) \leftarrow J$ of H$_2$O$\cdots$AgI and H$_2^{18}$O$\cdots$AgI) was approximately 3:1 in favour of the former. This strongly implies that H$_2$O$\cdots$AgI adopts either a geometry that is planar and of $C_{2v}$ symmetry at equilibrium or an alternative arrangement that has $C_s$ symmetry at equilibrium, a pyramidal configuration at O, but with a sufficiently low potential energy barrier to the planar $C_{2v}$ form that the wavefunction of the ground vibrational state has $C_{2v}$ symmetry. The orientation of the lone pair on the oxygen atom in the conventional model of the water molecule supports the second of these possibilities, leading to the equilibrium geometry of the general type shown in Fig. 3. This conclusion is corroborated by the ab initio calculations at the CCSD(T)/F12/AVTZ level of theory which find a
The experimentally determined geometry of H$_2$O···AgI drawn to scale (see Table V).

![Diagram](image)

**FIG. 3.**

The experimentally determined geometry of H$_2$O···AgI drawn to scale (see Table V).

**FIG. 4.**

The experimentally determined geometry of H$_2$N···AgI drawn to scale (see Table VI).

C. Molecular geometry

Figures 3 and 4, respectively, show the model geometries of the H$_2$O···AgI and H$_3$N···AgI complexes. Structural parameters in these models were directly fitted to moments of inertia using Kiesel’s STRFIT program$^{41}$ to yield $r_0$ results. For each of the two complexes, isotopic substitutions were available at all atoms except iodine, which permitted measurement of the spectra of six isotopologues of H$_2$O···AgI and eight isotopologues of H$_3$N···AgI. It was assumed that the $r_0$ geometries of the isolated H$_2$O and NH$_3$ monomers do not change on formation of each complex when determining the remaining $r_0$ structural parameters. The rationale for the described assumption has been presented previously.$^{10}$ Partial substitution structures ($r_s$) were also determined for H$_2$O···AgI and H$_3$N···AgI using Kraitchman’s equations.$^{42}$ The available isotopic data allow determination of $r_s$(Ag–O) = 2.232(2) Å for H$_2$O···AgI (Table V) and $r_s$(Ag–N) for H$_3$N···AgI = 2.182(1) Å (Table VI). Under the assumption that the geometry of the NH$_3$ sub-unit is unchanged from that in the $r_0$ geometry of H$_2$N, it is further possible to determine $\angle$(Ag–N–H) = 110.93(3)$^\circ$ for H$_3$N···AgI. The *ab initio* calculated geometries of H$_2$O···AgI and H$_3$N···AgI are also included in Tables V and VI, respectively. We note that the agreement between the observed and calculated angle $\angle$(Ag···X–H) is excellent for X = N but for X = O the experimental value of $\phi$ is smaller by 4$^\circ$. The poorer agreement in the case of X = O probably arises because the potential energy barrier to the inversion of configuration at O in H$_2$O···AgI is low (as it is in H$_2$O···AgCl$^{10}$ and H$_2$O···AgF$^{22}$) and therefore this motion makes a large amplitude contribution to the zero-point motion. The *ab initio* version of the angle is an equilibrium quantity and does not reflect such motion. On the other hand, the inversion is quenched in the case of X = N and there is no corresponding large amplitude contribution to the zero-point motion. We note that the experimental value of $\phi$ is smaller than its *ab initio* counterpart in each of H$_2$O···AgCl,$^{10}$ H$_2$O···CuCl,$^{10}$ and H$_2$O···AgF.$^{22}$

<table>
<thead>
<tr>
<th>TABLE V. r$_0$ and r$_e$ geometries of H$_2$O···AgI.</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(Ag–I) (Å)</td>
</tr>
<tr>
<td>r(Ag–O) (Å)</td>
</tr>
<tr>
<td>r(H–O) (Å)</td>
</tr>
<tr>
<td>$\phi$ (deg)</td>
</tr>
</tbody>
</table>

$^b$Calculated *ab initio* at the CCSD(T) (F12$^a$/AVTZ level.

D. Intermolecular stretching force constants

We recently proposed a model$^{43}$ that allows in principle some of the quadratic force constants of L···M–X complexes to be established from centrifugal distortion constants determined experimentally. This model goes beyond that of Millen,$^{44}$ by describing the centrifugal distortion constant $D_J$ (for symmetric top or linear complexes) or $A_J$ (for asymmetric-top complexes) in terms of three quadratic bond-stretching force constants $F_{11}$, $F_{22}$, and $F_{12}$, where the subscripts 1 and 2, respectively, refer to the M–X and L···M bonds (such that $F_{11}$ = $F_{M–X}$ and $F_{22}$ = $F_{L···M}$) with $F_{12}$ being the off-diagonal coupling term. The forms of the equations relating $D_J$ or $A_J$ to $F_{11}$, $F_{22}$, and $F_{12}$ are set out in detail in Refs. 7 and 43. If it is assumed that $F_{12}$ is zero, these equations reduce to Eq. (2) when applied to a molecule like H$_2$O···AgI having effectively $C_{2v}$ symmetry.

<table>
<thead>
<tr>
<th>TABLE VI. r$_0$, r$_s$, and r$_e$ geometries of H$_3$N···AgI.</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(Ag–I) (Å)</td>
</tr>
<tr>
<td>r(Ag–N) (Å)</td>
</tr>
<tr>
<td>r(H–N) (Å)</td>
</tr>
<tr>
<td>$\angle$(Ag–N–H) (deg)</td>
</tr>
</tbody>
</table>

$^b$Calculated *ab initio* at the CCSD(T) (F12$^a$/AVQZ level.
$$h \Delta J = \frac{\hbar^4}{4} \left[ \frac{1}{(I_{xx})^4} + \frac{1}{(I_{yy})^4} \right] \left( (m_1a_1)^2/F_{11} - (m_1a_1 + m_2a_2)^2/F_{22} \right),$$

(2)

where $m_{Ag}$ and $m_1$ are the appropriate nuclide masses, $a_{Ag}$ and $a_1$ are the principal axis coordinates of the Ag and I atoms and $I_{xx}$ and $I_{yy}$ are the equilibrium principal moments of inertia of the given isotopologue of $H_2O \cdots AgI$. Here it is assumed that zero-point quantities may be used in Eq. (2) without serious error. The corresponding form of Eq. (2) for $D_1$ of the symmetric-top molecule $H_3N \cdots AgI$ is obtained by setting $I_{bb} = I_{cc}$.

By assuming that $F_{11}$ is equal to the force constant of the isolated Ag–I diatomic molecule ($145.8 \text{ N m}^{-1}$), $F_{22}$ could be evaluated for $H_2O \cdots AgI$ and $H_3N \cdots AgI$ by fitting the appropriate centrifugal distortion constants. Data for the $^{14}N$ isotopologues were used in the case of $H_3N \cdots AgI$ because the absence of broadening through unresolved $^{14}N$ nuclear quadrupole hyperfine structure leads to more accurate values of $D_1$. The resulting values of $F_{22}$ are compared with the same quantity for several other molecular complexes of silver iodide in Table VII. Also included in Table VII are the corresponding quantities that arise from the use of the Millen model (these are referred to as $k_{orb}$ to use Millen’s nomenclature). It is clear that the Millen model severely underestimates this force constant, even for cases where the Lewis base is bound relatively weakly to the silver atom, as discussed in Refs. 7 and 43.

To inspect the sensitivity of $F_{22}$ to the assumption of unchanged $F_{11}$, $F_{22}$ was further evaluated over a range of $F_{11}$ values around that of free AgI. A plot showing the variation of $F_{22}$ with the force constant $F_{11}$ is displayed in Fig. 5. The horizontal asymptote (where $F_{11} \to \infty$) represents the case in which AgI can be regarded as rigid, and thus the value then obtained for the force constant $F_{22}$ is equal to that evaluated under the Millen model. The vertical asymptote ($F_{22} \to \infty$) represents the value of the force constant $F_{11}$ below which a negative (and therefore unphysical) value of $F_{11}$ is required to fit the centrifugal distortion constant. It is worth noting that the ordering of $F_{22}$ for these complexes is different depending on whether it is assumed that $F_{11}$ is equal to $145.8 \text{ N m}^{-1}$ (the value appropriate to the AgI diatomic molecule) or infinity (as would be implicit if M–X were approximated as a rigid diatomic molecule). By examining the slope of the curve near $F_{11} = 145.8 \text{ N m}^{-1}$, it can be seen that the sensitivity of $F_{22}$ to the value of $F_{11}$ changes greatly over the series of Lewis bases shown, with the highest sensitivity being $F_{11} \approx F_{22}$.

E. Electric charge redistribution across the Ag–I bond upon formation of $H_2O \cdots AgI$

The ionicity, $i_e$, or fractional ionic character of the iodine nucleus can be estimated from the expression

$$i_e = 1 + \frac{\chi_{ul}(I)}{eQq(I)},$$

(3)

where $eQq(5,1,0)(I)$ is the contribution to the iodine nuclear quadrupole coupling constant along the a inertial axis that arises from a single electron in an iodine $5p_a$ orbital and is equal to 2292.71 MHz. Table VIII compares the ionicities of the complexes studied here with those of other Lewis base-silver iodide complexes similarly obtained. For all these complexes, the ionicity of the Ag–X bond increases upon attachment of the Lewis base. The largest increases are observed for the $H_3P$, OC, $NH_3$ and $H_2S$ complexes, all lying between $i_e = 0.64$ and 0.68.

TABLE VII. Experimentally determined quadratic force constants, $F_{22}$, for L···AgI complexes (L = Ar, H,N, H,O, H,S, H,P, or CO).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$F_{22}$ (N m$^{-1}$)</th>
<th>$k_{orb}$ (N m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar···AgI$^a$</td>
<td>20.2(8)</td>
<td>14.8</td>
</tr>
<tr>
<td>H$_2$O···AgI$^a$</td>
<td>83(3)</td>
<td>13.9</td>
</tr>
<tr>
<td>H$_3$N···AgI$^a$</td>
<td>92.0(17)</td>
<td>29.0</td>
</tr>
<tr>
<td>H$_3$P···AgI$^a$</td>
<td>122(5)</td>
<td>31.7</td>
</tr>
<tr>
<td>OC···AgI$^a$</td>
<td>156(26)</td>
<td>47</td>
</tr>
<tr>
<td>H$_3$N···AgI$^b$</td>
<td>192(38)</td>
<td>15.1</td>
</tr>
</tbody>
</table>

$^a$Calculated by using the two-force constant model to fit $D_1$ values, assuming $F_{11} = 145.8 \text{ N m}^{-1}$, the value for free AgI in its vibrational ground state. Numbers in parentheses are one standard deviation of the fit in units of the last significant figures.

$^b$Values were determined from $D_1$ values by means of the model described by Millen (Ref. 44).

TABLE VIII. Ionicity of Ag–I in L···AgI complexes (where L = Ar, H,N, H,O, H,S, H,P, or CO).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\chi_{ul}(I)$ (MHz)</th>
<th>$i_e$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–I</td>
<td>$-1062.5299(15)^b$</td>
<td>0.537</td>
</tr>
<tr>
<td>Ar···AgI$^c$</td>
<td>$-985.411(54)$</td>
<td>0.570</td>
</tr>
<tr>
<td>H$_2$O···AgI$^c$</td>
<td>$-885.54(11)$</td>
<td>0.613</td>
</tr>
<tr>
<td>H$_3$N···AgI$^c$</td>
<td>$-807.36(4)$</td>
<td>0.648</td>
</tr>
<tr>
<td>H$_3$P···AgI$^c$</td>
<td>$-795.42(54)$</td>
<td>0.65</td>
</tr>
<tr>
<td>OC···AgI$^c$</td>
<td>$-769.84(22)$</td>
<td>0.66</td>
</tr>
<tr>
<td>H$_3$P···AgI$^c$</td>
<td>$-733.83(34)$</td>
<td>0.68</td>
</tr>
</tbody>
</table>

$^a$Calculated using Eq. (3) and $eQq(5,1,0)(I)$ values cited in Ref. 43.

$^b$Reference 35.

$^c$Reference 17.

$^d$Reference 3.

$^e$Reference 9.

$^f$Reference 7.
whereas $i_c$ for isolated AgI is 0.537. The complex with H$_2$O causes a smaller increase in the ionicity of the Ag–X subunit.

This is different from the trend observed when these Lewis bases bind to silver chloride.\textsuperscript{4,10,17} The ordering of the $i_c$ values displayed in Table VIII is also different from the ordering of complexes according to the value of the force constant, $F_{22}$. It might be expected that the change in charge distribution across the Ag–I bond upon attachment of a Lewis base, as measured by the change in nuclear quadrupole coupling constant, will be approximately proportional to the strength of the interaction of the Lewis base with the silver atom. Whilst this is generally true for the complexes listed in Tables VII and VIII, there are some notable exceptions. The force constant ($F_{22}$) of the bond formed between water and silver iodide is similar in magnitude to that for the intermolecular bond in H$_2$S···AgI but has a very similar value of $i_c$ for the corresponding complexes span a relatively wide range from 0.61 to 0.65. Likewise NH$_3$ is calculated to bind more strongly to the silver atom in AgI ($F_{22} = 192(38)$ N m$^{-1}$) than does H$_2$S to Ag in H$_2$S···AgI ($F_{22} = 92.0(1.7)$ N m$^{-1}$) but has a very similar value of $i_c$.

IV. CONCLUSIONS

Two Lewis base-silver iodide complexes, L···AgI (L = H$_2$N and H$_2$O), have been generated through laser vaporisation of a solid target in the presence of a gas sample undergoing supersonic expansion and characterized by pure rotational spectroscopy. The basic geometries of the complexes studied are qualitatively the same as those established previously for several other members of the L···AgCl series. The values of $r$(Ag–O) and $\varphi$ for H$_2$O···AgCl are 2.229(35) Å and 42(5)$^\circ$, respectively, whereas those for H$_2$O···AgI are 2.227(7) Å and 36.3(12)$^\circ$, respectively. Comparing results for H$_2$N···AgCl and H$_2$N···AgI, the values of $r$(Ag–N) are 2.154 44(6) Å and 2.180(1) Å, respectively. Evidently, the identity of the halogen atom has only a small effect on structural parameters associated with interactions between L and AgX sub-units. It has previously been noted that $\varphi$ for H$_2$O···AgCl is very similar in magnitude to an equivalent parameter in the geometry of H$_2$O···HCl and H$_2$O···CuCl. These observations are all therefore consistent with a model in which the geometry of each complex is principally determined by the orientation of the lone pair on the oxygen atom which aligns with the axis of the bond in the electrophile acting as the Lewis acid.

SUPPLEMENTARY MATERIAL

See supplementary material for the final cycle of the fit to the ground-state rotational spectrum of each reported isotopologue of H$_2$N···AgI and H$_2$O···AgI using PGOPHER and the spectroscopic constants thereby determined.

ACKNOWLEDGMENTS

The authors thank the European Research Council for a postdoctoral fellowship awarded to C.M., a Ph.D. studentship awarded to J.C.M., and for project funding (Grant No. CPFTMW-307000); Newcastle University for Ph.D. studentships awarded to D.M.B. and E.G. The University of Bristol is thanked for a Senior Research Fellowship awarded to A.C.L. S.B. thanks the Ministerio de Educación, Cultura y Deporte of Spain, “Salvador de Madariaga” program, for financial support.