Monohydrate of argentous fluoride: $H_2O \cdots AgF$ characterised by rotational spectroscopy and ab initio calculations

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ABSTRACT

Pure rotational spectra of the ground vibrational states of eight isotopologues of $H_2O \cdots AgF$ have been measured and analysed to determine rotational and centrifugal distortion constants. The molecular structure and spectroscopic parameters determined from the experimental data are presented alongside the results of calculations at the CCSD(T) level. Both experiment and theory are consistent with structures that are non-planar at equilibrium. In the determined r_0 geometry, the heavy atoms are collinear while the local C_2 axis of the water molecule intersects the axis defined by the heavy atoms at an angle, ϕ = 41.9(11)°. The equilibrium geometry thus has C_s symmetry. In the zero-point state, however, the molecule is effectively planar, undergoing rapid inversion between two equivalent structures where ϕ has equal magnitude but opposite sign. The ab initio calculations confirm that the timescale of this inversion is at least an order of magnitude faster than that of rotation of the molecule in the lowest rotational energy levels. The molecular geometries are rationalized using simple rules that invoke the electrostatic interactions within the complexes.

1. Introduction

Recently, we have been making systematic investigations of a type of pairwise interaction involving closed-shell molecules that has parallels with the more familiar hydrogen- and halogen-bond interactions but is generally stronger [1–5]. The interaction in question is that between a Lewis base B and a diatomic molecule M–X, where M is a Group 11 coinage metal (Cu, Ag or Au) and X is a halogen.

To allow direct comparison of the measured properties of the B···M–X molecules with those from ab initio calculations, experimental investigations in the gas phase are desirable but the involatile nature of the coinage metal halides M–X and the relatively weak B···M bond make it difficult to produce M–X in the gas phase by conventional methods. However, Gerry [6–11] and co-workers have developed an elegant method by which the gas-phase metal halide M–X is produced *in situ* by laser ablation of the metal M in the presence of a gas-phase source of halogen atoms X and the Lewis base B. Some of the M–X molecules so produced then pick up a molecule of B to give B···M–X. Gerry and co-workers used either an inert gas atom or CO as the Lewis base [7–11], while so far we have employed N_2, CO, H_2O, H_2S and NH_3 in this capacity [1–5].

We report here the first synthesis and characterisation of $H_2O \cdots Ag–F$ which was produced by ablating metallic silver in the presence of SF_6 (the source of F atoms) and H_2O contained in excess argon. The rotational spectrum of $H_2O \cdots Ag–F$ so generated was recorded with a pulsed-jet, Fourier transform microwave spectrometer and the spectroscopic constants obtained from spectral analysis were interpreted to give the geometry and one measure of the interaction strength of the two molecules forming this novel compound. These properties are compared here with those generated ab initio at the CCSD(T)/cc-pVQZ level of theory and with those obtained experimentally for the hydrogen- and halogen-bonded complexes $H_2O \cdots HF$, $H_2O \cdots F_2$ and $H_2O \cdots ClF$ [12–14].

2. Experimental

A gaseous sample containing ~1% SF_6 (Fluorochem), 99% argon and a small concentration of H_2O is initially pulsed from a nozzle (General Valve, Series 9) using a backing pressure of 6 atm. This gas pulse passes over a silver rod which is ablated by the pulsed output from the second harmonic (532 nm) of a Nd:YAG laser to yield gaseous silver atoms and ions. The delay between the gas and laser pulses is adjusted to maximise the abundance of $H_2O \cdots AgF$ generated within the supersonically-expanding gas. The rod target is continuously rotated and translated to expose a clean surface to each laser pulse ensuring greater signal intensity and reproducibility.

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The SF_6 within the gas sample acts as a precursor of fluorine atoms. The preferred method for introducing water involves addition of a single drop into the tube carrying the pressurised gas sample to the nozzle. Compared with various alternatives, this method was found to yield optimal signal intensities while also requiring the lowest water consumption allowing observations to be performed on isotopologues containing isotopically-enriched samples of $D_2^{16}O$ (Aldrich, 99%) and $H_2^{18}O$ (Isotec Inc. 97.5%). Enriched samples of $HD^{16}O$ were prepared from equal volumes of $D_2^{16}O$ and $H_2^{16}O$ and allowing these to mix over 24 h. A silver rod target (Goodfellow, 99.95%) containing [107]Ag and [109]Ag in natural abundance was used to record the majority of the data. It will be shown that the silver atom is very close to the centre of mass in $H_2O\cdots AgF$ and that substitution of the silver atom causes only a very small change in the rotational constants of the molecule. For this reason, the spectrum of a given isotopologue cannot be unambiguously assigned to the correct isotope of silver from the measured rotational constants alone. The natural abundance of the two isotopes of silver is approximately equal, yielding rotational transitions which have approximately the same intensity. Given that neither [107]Ag nor [109]Ag possess quadrupolar nuclei, it is also not possible to exploit nuclear quadrupole coupling to make the correct assignment of the silver isotope. Isotopically enriched [107]Ag (CK gas products 99.6% [107]Ag, 0.4% [109]Ag) was used to assign correctly and unambiguously the isotope of silver to each of the isotopologues that yield the observed spectra. This sample was available as irregularly-shaped pieces of thin film which were fixed to a glass rod to serve as the ablation target. The measured transitions of $H_2O\cdots AgF$ were generally lower in intensity than those observed in comparable studies [5,11] of $H_2O\cdots AgCl$, $H_2O\cdots CuCl$ and $OC\cdots AgF$. It is possible that the latter species are formed from the various precursors within the plasma with greater efficiency than $H_2O\cdots AgF$.

The jet containing $H_2O\cdots AgF$ subsequently enters the Fabry–Perot cavity of a Balle–Flygare Fourier transform microwave (FTMW) spectrometer. This spectrometer has been described in previous works [15,16], therefore only a brief description will be provided here. Each of the two spherical aluminium mirrors has a diameter of 35 cm and a radius of curvature of 84 cm. The separation between the two mirrors is approximately 70 cm and variable to allow tuning of the cavity modes to frequencies between 6 and 18 GHz. The bandwidth of the cavity is ~0.5 MHz. The microwave excitation pulse is transmitted a short time (~1.40 ms) after supersonic expansion of the gas pulse into the Fabry–Perot cavity. Molecules are polarised by the microwave pulse if the transition from the lower state is resonant or nearly resonant with the radiation and subsequently undergo spontaneous coherent emission at the transition frequency. The molecular free induction decay is digitised, summed and Fourier-transformed to yield the power spectrum. A repetition rate of 4 Hz is used. The data can be averaged over an extended period of time to ensure a satisfactory S/N ratio for measurements. All frequencies are referenced to a 10 MHz external source with an accuracy better than 1 part in 10^{11} (Symmetricom 58533A, GPS time and frequency receiver). Resolution of the molecular transitions is enhanced because the molecular microwave emission is detected coaxially with the velocity of the supersonic jet. Each molecular transition is observed as a pair of Doppler components and averaging these provides the molecular transition frequency.

3. Computational details

All calculations were performed using the Molpro package [17]. Coupled-cluster singles and doubles theory with a perturbative treatment of triples, CCSD(T), was used to evaluate points on the potential energy surface and to locate the stationary points. The frozen core approximation was applied. Calculations were performed using VTZ and VQZ basis sets, where the short hand VTZ refers to the following combination of basis sets: For $H_2O\cdots AgF$, the cc-pVTZ basis was used for the H, O and F atoms. The cc-pVTZ-PP basis was used for the Ag atom where a pseudo potential was adopted to account for scalar relativistic effects [18–20]. The basis set represented by the short hand VQZ is defined in a completely analogous way to the VTZ basis, simply replacing 'T' with 'Q'. The counter-poise correction due to Boys and Bernardi [21] was used to compute the binding energies, but was not used in the computation of the potential energy curves, where basis set superposition errors are expected to be relatively small.

4. Results and discussion

4.1. Detection and observation of rotational transitions

Recent work [3,5] has shown that the structure of $H_2O\cdots AgCl$ is effectively C_{2v} with a collinear arrangement of oxygen, silver and chlorine atoms. The equilibrium geometry of the complex has C_s symmetry. The local C_2 axis of the water molecule intersects the axis defined by the heavy atoms to define an angle, ϕ. The structure of $H_2O\cdots AgF$ was initially assumed to resemble the C_s equilibrium geometry of $H_2O\cdots AgCl$. The qualitative features of this model are illustrated in Fig. 1. The results of the ab initio calculations supported this assumption and also informed the starting point for a search for the $1_{01} \leftarrow 2_{02}$ rotational transition of the $H_2^{16}O\cdots^{107}AgF$ isotopologue.

Following a brief search, a pair of transitions was identified at a frequency of ~12 294 MHz (Fig. 2). It was established that these transitions required both the laser pulse (providing silver) and the simultaneous presence of SF_6 and H_2O in the gas sample. Consistent with the assignment of two distinct $H_2O\cdots AgF$ isotopologues as the molecular carriers of these transitions, further searching yielded no evidence of hyperfine splitting in the rotational transitions. The fact that the two transitions are within a few kilohertz of each other indicates that the silver atom is very close to the centre of mass in this molecule. Further transitions were identified at frequencies near to ~18 441 MHz allowing each of the spectra to be assigned to either $H_2^{16}O\cdots^{107}AgF$ or $H_2^{16}O\cdots^{109}AgF$. Extending the comparison with $H_2O\cdots AgCl$, it was expected that either a low barrier to inversion exists between two structures of C_s symmetry where ϕ (as defined in Fig. 1) has equal magnitude but opposite sign or the molecule is planar at equilibrium (i.e. $\phi = 0$). Under these circumstances which have been observed [3,5] to apply to $H_2O\cdots AgCl$, the two vibrational levels with lowest energy are well separated. Efficient cooling in the supersonic expansion results in rapid relaxation to the lowest vibrational energy level. Collisional propensity rules inhibit further relaxation from levels with $v = 0^+$, $K_{-1} = 1$ to $v = 0^+$, $K_{-1} = 0$ resulting in a significant population of molecules remaining with $v = 0^+$, $K_{-1} = 1$. Consequently, transitions involving $K_{-1} = 1$ are observed
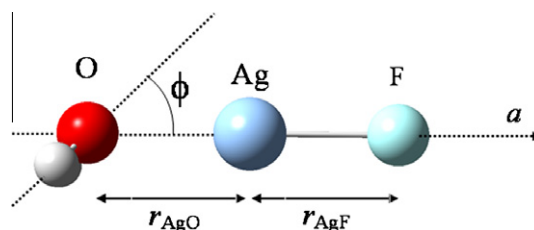

Fig. 1. The structural model applied to interpret the spectra of $H_2O\cdots AgF$. The a inertial axis is indicated and the structural parameters are defined as shown. The a inertial axis is very nearly aligned with the axis defined by the heavy atoms, O, Ag and F.