The halogen bond between ethene and a simple perfluoroiodoalkane: C₂H₄···ICF₃ identified by broadband rotational spectroscopy

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ABSTRACT

An isolated complex of C_2H_4 and ICF_3 has been generated in the gas phase and studied by chirped-pulse, Fourier transform microwave (CP-FTMW) spectroscopy. *Ab initio* calculations at the CCSD(T)(F12*)/VTZ level support the experimental work and further establish the dissociation energy, D_e, and dipole moment, μ, of the complex. Rotational constants, B_0 and C_0, the centrifugal distortion constant, Δ_J, nuclear quadrupole coupling constants, χ_{aa} (I) and $(\chi_{bb}(I)-\chi_{cc}(I))$ and the nuclear spin-rotation coupling constant C_{bb}(I) of the complex are determined from the experimental data. The iodine atom interacts with π-electrons on C_2H_4 resulting in the formation of a linear $(\angle(C-I\cdots*))$ halogen bond (where $*$ indicates the centre of the C=C bond) and a complex of C_s symmetry. The measured rotational constants allow the length of the halogen bond to be determined as 3.434(2) Å in the r_0 geometry. The complex is formally an asymmetric top but with a very low barrier to internal rotation of C_2H_4 about the C_3 axis defined by the CF_3I sub-unit. Adopting an approach also used in a recent study of $H_2O\cdots ICF_3$, other transitions are assigned using the Hamiltonian of a symmetric top molecule.

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1. Introduction

Pre-reactive complexes can be prepared and characterised in the cold environment of a supersonic jet to provide insight into intermolecular interactions. Recent work [1–3] in our group has examined complexes that contain prototypes of halogen bonding interactions that are significant in crystal engineering. Iodoalkanes and iodoperfluoroalkanes are attractive intermediates for use in synthetic chemistry owing to the ability of an iodine substituent to act as a leaving group [4]. Thermal or photochemical initiation of the reaction between CF_3I and C_2H_4 involves addition of the alkene into the C—I bond yielding $CF_3(CH_2)_2I$ as a product [5]. This process can provide the initial step in radical polymerisation reactions. For these reasons, the interaction between CF_3I and C_2H_4 is of fundamental interest and this work explores the nature of the halogen bond in an isolated complex formed of these two monomers.

It was recently shown that the complexes formed between CF_3I and each of NH_3 and $N(CH_3)_3$ respectively contain halogen bonds, I···N, with linear C—I···N arrangements of atoms [2]. The length of the halogen bond in $(CH_3)_3N\cdots ICF_3$ is very similar to that associated with N···I halogen bonds in crystal structures. Spectra of OC···ICF₃ and Kr···ICF₃ were interpreted to reveal similarities [3] between trends in B···ICl (where B is a simple Lewis base) and

B···ICF₃. The described OC···ICF₃, Kr···ICF₃, H₃N···ICF₃ and $(CH_3)_3N\cdots ICF_3$ complexes are either linear or symmetric tops containing a linear halogen bond such that $\angle(C-I\cdots B)$ is equal to 180°. Complexes [1] of $H_2S\cdots ICF_3$ and $H_2O\cdots ICF_3$ were studied to reveal equilibrium geometries consistent with asymmetric top structures and linear halogen bonds. As a consequence of nearly-free internal rotation of H_2S relative to CF_3I, the protons in $H_2S\cdots ICF_3$ are highly delocalised around the C—I···S axis and the spectrum of this complex was assigned by assuming a Hamiltonian appropriate to a symmetric top molecule. The obtained spectrum of $H_2O\cdots ICF_3$ could not be interpreted using a standard Hamiltonian. Consistent with previous studies [6] of $H_2O\cdots CF_4$ and $H_2O\cdots ClCF_3$, it is believed that internal dynamics significantly affect the observed spectrum of $H_2O\cdots ICF_3$. The present work will show that the spectrum of $C_2H_4\cdots ICF_3$ presents similar challenges to assignment. It will determine the length of the halogen bond in the complex and compare this with that found [7] in $C_2H_4\cdots ICl$. It will be shown that the CP-FTMW (chirped-pulse Fourier transform microwave) technique [8] provides an unparalleled experimental tool for the measurement of rotational spectra, particularly where these defy simple interpretation. Aside from the articles published in this special issue, results obtained through CP-FTMW spectroscopy are the subject of a recent review article [9].

Halogen-bonded interactions with non-aromatic π-systems in solution were the subject of a recent investigation [10] by Hauchecorne et al. where Fourier transform infrared spectroscopy, Raman spectroscopy and *ab initio* calculations were deployed to determine

bond lengths and vibrational frequencies. It was calculated that the length of the halogen bond is 3.45 Å and that the angle, $\angle$(C—I$\cdots$*) is 180 in $C_2H_4\cdots ICF_3$. It was found that increases in the lengths of the C—F, C—I and C=C bonds on formation of the $C_2H_4\cdots ICF_3$ complex are 0.0026 Å, 0.0023 Å and 0.0027 Å respectively. It was noted that the complexation enthalpy of $C_2H_4\cdots ICF_3$ is −8.8(1) kJ mol^{-1} and significantly lower than the same quantity in complexes of $(CH_3)_2O\cdots ICF_3$, $(CH_3)_2S\cdots ICF_3$ and $(CH_3)_3N\cdots ICF_3$. It is lower than the complexation enthalpy determined for $C_3H_6\cdots ICF_3$ though higher than that determined for $C_2H_4\cdots BrCF_3$. The present work explores the $C_2H_4\cdots ICF_3$ complex isolated in the gaseous phase through broadband rotational spectroscopy and *ab initio* calculations. Rotational constants, centrifugal distortion constants, nuclear quadrupole coupling constants and the length of the halogen bond are determined.

2. Experimental

A comprehensive description of the CP-FTMW spectrometer [11] is provided in a recent work and only a brief description is given here. An arbitrary waveform generator (Tektronix, AWG7102B) is used for the initial generation of a chirped microwave pulse that sweeps from 0.5–12 GHz over a period of 1 μs. This chirped pulse is passed through a low-pass filter (12.2 GHz, Lorch 11LA-12200-s) and mixed against the output of a phase-locked dielectric resonant oscillator (Herley CTI, XPDRO-14373) that supplies a 19.00 GHz signal. The AWG and PDRO are each phase-locked to a 10 MHz frequency reference (Symmetricom 58533A, GPS time and frequency reference receiver) accurate to 1 part in 10^{11}. The output after mixing (7–18.5 GHz) is amplified prior to irradiation of the molecular sample. The data presented herein were acquired using a 300 W travelling wave tube amplifier (Amplifier Research, 300IJ) in place of the 5 W solid-state amplifier described previously. This 300 W amplifier permits the transitions of $C_2H_4\cdots ICF_3$ to be simultaneously measured across a 11.5 GHz bandwidth.

A gas sample of ∼1% CF_3I and the same proportion of C_2H_4 is prepared in a balance of ∼98% argon at a backing pressure of 1 atm. A small amount of this sample is pulsed from a nozzle (Series 9, General Valve) such that $C_2H_4\cdots ICF_3$ is formed in the cold environment of the expanding supersonic jet and travels perpendicular to the propagation of the microwave polarisation pulse transmitted from a horn antenna. The repetition rate of gas pulses is approximately two hertz. The microwave pulse is timed to ensure spatial and temporal overlap with the gas pulse. A pin diode limiter and single-pole, single-throw (SPST) pin diode switch are used to protect the low noise amplifier used in the detection circuit from the high power of the polarisation pulse. The SPST switch is subsequently opened to allow measurement of the molecular free induction decay which follows the microwave polarisation pulse. Microwave-absorbent, carbon-loaded polyurethane foam (Emerson and Cuming, Eccosorb HR-1) covers the inside surfaces of the vacuum chamber to accelerate the decay of reflected components of the chirped excitation pulse and reduce their interference with the molecular free induction decay. The duration of the nozzle pulse is between 200 and 250 μs and significantly greater than that of the polarisation pulse (1 μs) and the molecular free induction decay (∼20 μs). It is thus possible to polarise molecules in the gas pulse and detect the subsequent free induction decay (FID) repeatedly within the duration of each gas injection pulse. In the present work, eight chirped pulses separated by an interval of ∼21 μs are used to polarise repeatedly the molecules within each gas pulse.

The molecular emission signal is detected by a second horn antenna and amplified by a low noise amplifier. The FID is mixed down against the 19.00 GHz reference signal supplied by the PDRO. Each FID is measured over a 20 μs period following each chirped polarisation pulse. A digital oscilloscope (Tektronix, DPO71254) of 12.5 GHz bandwidth is used to digitise the molecular emission signal and perform the Fourier transformation that allows the power spectrum of each FID to be displayed. The train of eight FIDs detected following every nozzle pulse is averaged in the time domain. At the conclusion of data collection, this train of eight time-averaged FIDs is displayed on the oscilloscope. Each of these is then Fourier transformed individually before the resulting power spectra are summed in the frequency domain. The oscilloscope is phase-locked to the same 10 MHz external frequency reference used by the PDRO and AWG. Observed transitions have a linewidth (full width at half maximum) of approximately 80 kHz.

3. Computational details

The structure of $C_2H_4\cdots ICF_3$ is optimised at the CCSD(T) level of theory [12], that is, coupled-cluster singles and doubles with a perturbative treatment of triple excitations. Calculations are performed using double and triple zeta quality basis sets composed of the cc-pVXZ basis sets for C and H [13], aug-cc-pVXZ for F and the cc-pVXZ-PP basis set for I [14], where PP indicates that a 28-electron pseudo-potential was used to account for relativistic effects in the I atom and X=D or T. Only valence electrons are included in the correlation treatment. To further converge the structural parameters with respect to the size of the basis set, explicitly-correlated calculations are performed using the CCSD(T)(F12∗) method and the MOLPRO and Turbomole program packages [15–18]. Furthermore, the CCSD(T)(F12∗)/VTZ method was used to compute the $C_2H_4\cdots ICF_3 \rightarrow C_2H_4 + ICF_3$ dissociation energy and the electric dipole moments of the complex and fragments. Harmonic frequencies were computed using the CCSD(T)(F12∗)/VDZ method at the CCSD(T)(F12∗)/VDZ optimised geometry.

4. Results and data analysis

4.1. Spectroscopic analysis of $C_2H_4\cdots ICF_3$

Fig. 1 displays the spectrum obtained when probing all molecules and complexes present in the expanding gas pulse. The most intense transitions assign readily to the CF_3I monomer which is abundant within the prepared sample. Less intense features are observed at regular frequency intervals smaller than those separating the rotational transitions of CF_3I. These new features were not observed during earlier experiments that used CF_3I and are only seen when C_2H_4 is present within the gas sample. The observations
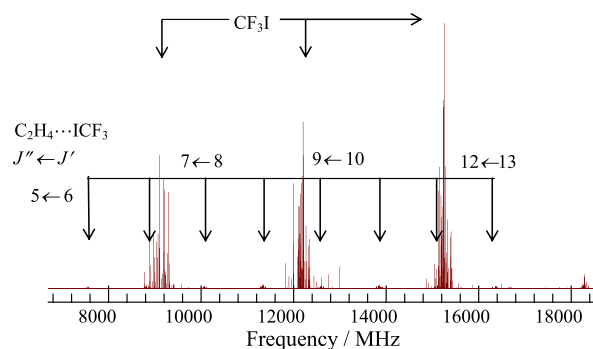

Fig. 1. Broadband rotational spectrum of the gas sample that contains CF_3I, C_2H_4 and Ar. The most intense features in the spectrum assign to CF_3I. Features attributed to $C_2H_4\cdots ICF_3$ are indicated.