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Observation and quantification of the hydrogen bond effect on O–H overtone intensities in an alcohol dimer

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Abstract

First overtone ($2\nu_{OH}$) transitions of the two OH-stretching modes in isolated 2,2,2-trifluoroethanol dimers are observed for the first time. Their relative intensities provide quantitative evidence for the pronounced IR intensity suppression of two-quantum hydrogen-bonded OH-stretching excitations relative to fundamental transitions by up to three orders of magnitude. The OH anharmonicity is shown to increase by 15% upon hydrogen bonding to another oxygen, whereas it remains constant upon hydrogen bonding to a fluorine atom. The experimental results are supported by reduced-dimensionality anharmonic calculations in up to three dimensions.
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1. Introduction

Hydrogen bonding can increase the IR oscillator strength of OH-stretching fundamentals by more than an order of magnitude [1]. It has been noted repeatedly over the last decades that this increase is largely absent in the corresponding first overtone transitions [2,3]. It may even turn into an intensity decrease, compared to the free OH group. Simple explanations have been given [4–6]. They involve the curvature of the dipole moment function and mechanical anharmonicity. Their interplay cancels the strong enhancement present in the fundamental range in a fairly systematic way for overtone vibrations within strong hydrogen bonds. For weak hydrogen bonds, the effects may be less pronounced [5], but even for C–H bonds [7], the overtone intensity of the hydrogen-bonded complex can be significantly smaller than that of the isolated molecule [6,8].

A quantitative demonstration of this phenomenon for vacuum isolated hydrogen bonds between organic molecules appears to be missing. First overtone transitions have been observed in isolated hydrogen fluoride dimer [9–11], HCN dimer [12], water dimer [13] and protonated water clusters [14], but no detailed intensity analysis relative to fundamental transitions was performed. In HF dimer, approximately comparable band strengths for the donor and acceptor overtone vibrations were observed [11]. For HCN–HF, a rather comprehensive experimental characterization of the anharmonic force field has been carried out [15], but again, no intensity analysis was attempted to compare with theoretical predictions [16,17]. Overtones of molecules with intramolecular hydrogen bonds have been observed at thermal equilibrium in the gas phase [18,19] and in solution [20]. Intermolecular examples were usually studied in condensed phases, either in solution [21], including cryosolutions [6], or in matrix isolation [22,23], but circumstantial evidence in the hot or room temperature gas phase was recently also presented for methanol–trimethyl-amine [24] and glycolic acid–water [19]. In the case of HF dimer in a neon matrix, the donor overtone is attenuated

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by a factor of ≈ 300, whereas the acceptor overtone is only attenuated by a factor of ≈ 20, relative to the corresponding fundamental transitions [23]. However, there are significant discrepancies with respect to gas phase measurements, where available, and with respect to theoretical estimates [23]. The direction of these discrepancies differs from that found for related systems in He droplets [25] and it is unclear whether they are due to the matrix or due to deficiencies in the theoretical treatment of electron correlation and mechanical as well as electrical anharmonicity. This calls for experimental overtone data in the low temperature gas phase, where matrix embedding effects are absent.

The infrared absorption cross-section of hydrogen-bonded complexes is sometimes claimed to be relevant for the radiation balance of the atmosphere [26,5]. As the atmospheric detection of such complexes is difficult in the fundamental range, there have been attempts to observe them in the less congested overtone region [27,28]. In this context, laboratory measurements under optimized conditions can be useful [29]. Overtone frequencies are of course also important to determine experimental anharmonicity constants. Alternative routes via deuteration effects [22,30] are less accurate [31], but qualitatively useful in the absence of sufficiently strong overtone transitions [32,33].

Here, we present the first observation of OH-stretching overtones in jet-cooled alcohol dimers. We have chosen the dimer of 2,2,2-trifluoroethanol (TFE) as a prototype system for several reasons (Fig. 1). It was previously shown to relax into a single conformation upon jet cooling [34,33], despite many conformational possibilities. It contains both a classical OH$\cdots$O and a weaker OH$\cdots$F intermolecular hydrogen bond, which allows for a direct and unbiased intensity comparison within the dimer. In the OH-stretching fundamental range, the infrared bands are exceptionally narrow [34], promising a well-resolved overtone spectrum as well. Furthermore, the vapor pressure of TFE is sufficiently high to allow for a good cluster signal-to-noise ratio in the supersonic expansion [35]. Finally, the vibrational dynamics of the OH oscillator in TFE is of
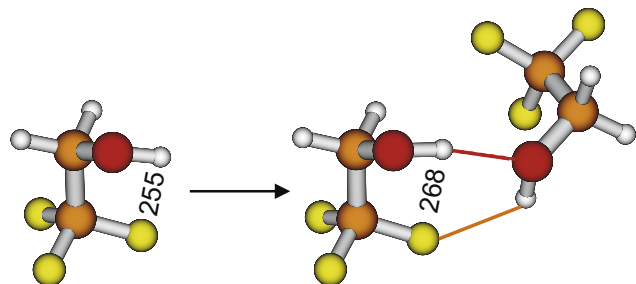
interest in itself, because this amphiphilic molecule serves as a co-solvent in peptide folding studies [36].

To analyze the experimental overtone spectrum, we have carried out reduced-dimensionality variational calculations involving between one and three normal modes. They build on potential energy and electric dipole moment hypersurfaces computed at the MP2/6-311+G* level by successively averaged spline interpolation (SASI) [37,38]. The discrete variable representation (DVR) of the vibrational Hamiltonian allows for the fully coupled anharmonic calculation of overtone spectra [39], here in up to three dimensions.

2. Methods

The infrared spectra were recorded at 2 cm^{-1} resolution (0.5 cm^{-1} for control experiments) with a Bruker Equinox 55 FT-IR spectrometer equipped with a tungsten lamp, a CaF$_2$ beamsplitter and a large area liquid nitrogen-cooled InSb detector (Judson). The collimated IR beam of ≈ 35 mm diameter was focussed by a $f = 500$ mm CaF$_2$ lens into a vacuum chamber of 776 mm cross-section. The diverging IR beam was recollimated by a $f = 250$ mm CaF$_2$ lens at the end of the vacuum path and focussed on the detector using an off-axis parabolic mirror. The convergent–divergent beam section in the vacuum chamber crossed the zone of silence of a 1 bar pulsed supersonic jet expansion emerging from a parallel 600 mm $\times$ 0.2 mm slit nozzle. The optical axis was positioned 10 mm downstream the nozzle exit. Gas pulses of about 0.3 mol He (Air liquid, 99.996%) containing 0.06–0.36% TFE (ABCR, 99%) were generated by six magnetic valves of 8 mm nominal width (Parker Lucifer) which filled a pre-expansion chamber of 0.5 dm^3 volume. Single gas pulses were synchronized to full interferometer scans of 0.10 s duration. Buildup of excessive background pressure during the gas pulse was prevented by the size of the vacuum chamber (23 m^3). Before the next gas pulse was triggered, the chamber was evacuated down to 0.1 mbar within 35–45 s using a series of rotary lobe pumps with a total pumping speed up to 2500 m^3/h. Further details of the experimental setup (filet-jet) are given elsewhere [40,35].

In the fundamental OH-stretching range, co-addition of the spectra from 150 gas pulses at a concentration of 0.06% TFE in He was sufficient, because an optical filter from 2.5 μm to 3.5 μm prevented shot-noise from non-relevant spectral regions and allowed for a spectrometer aperture of 3.5 mm. In the overtone range, where the photon flux was lower and the integrated absorption cross-section (integrated absorption coefficient) up to 800 (400) times smaller, a narrow-band filter (1.4–1.5 μm) was used and spectra from 600 gas pulses had to be co-added despite the use of a more concentrated TFE/He gas mixture (0.36%). Further improvements can be expected with appropriately matched InGaAs or Ge detectors [15]. Fundamental spectra under identical conditions as the overtone spectra were recorded by switching the optical filter and leaving all other parameters unchanged. The fundamental spectrum shown in the

Fig. 1. Structure of the most stable conformation of TFE (left) and its dimer (right), which involves a strong OH$\cdots$O (red) and a weak OH$\cdots$F (orange) intermolecular hydrogen bond. The intramolecular H$\cdots$F distance in pm at MP2/6-311+G*-level is indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)