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STUART A. RICE

ADVANCES IN CHEMICAL PHYSICS

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VOLUME 142

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CONTRIBUTORS TO VOLUME 142

BENJAMIN AUER, Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

BJÖRN H. JUNKER, Leibniz Institute of Plant Genetics and Crop Plant Research, 06466 Gatersleben, Germany

YU-SHAN LIN, Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

JAMES L. SKINNER, Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

RALF STEUER, Manchester Interdisciplinary Biocentre, School of Chemical Engineering and Analytical Science, University of Manchester, Manchester M17DN, United Kingdom

MARTIN A. SUHM, Institut für Physikalische Chemie, Universität Göttingen, Göttingen, 37077 Deutschland, Germany

INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

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HYDROGEN BOND DYNAMICS IN ALCOHOL CLUSTERS

MARTIN A. SUHM

Institut für Physikalische Chemie, Universität Göttingen, 37077 Göttingen, Germany

CONTENTS

I. INTRODUCTION

Alcohols are the conceptually simplest organic molecules that undergo classical hydrogen bonding. Given the enormous importance of hydrogen bonding in complex organic and biological matter [1, 2], it is imperative to understand its dynamics for such simple, yet realistic, model systems. By adding one molecule at a time, the evolution from single molecules to condensed phases can be mapped out in a molecular cluster approach [3]. In contrast to the more elementary, more abundant, but completely singular water system [4], alcohols can be tailored by modifying their molecular backbone [5]. This "chemical" dimension renders them particularly valuable for supramolecular design [6]. In terms of hydrogen bond topology, it is the reduced dimensionality which makes alcohols attractive. Compared to the complex three-dimensional network present in water, the propensity for ring and chain aggregation in alcohol clusters [7] provides an elementary starting point for the investigation of energy flow along a sequence of intermolecular interactions [8], with important applications in solution and neat liquid phases [9–11]. The coexistence of hydrophobic and hydrophilic domains also leads to interesting surface effects [12] and microstructure in liquid alcohols [13], quite in contrast to water. Alcohols are clearly among the most elementary and longest known [14] protagonists in gas-phase supramolecular chemistry [15].

A dedicated review on hydrogen bonding in isolated alcohol clusters bridging methanol on one side [16] and sugars on the other [17] appears timely. In 1996, there were about 12 citations to publications including the keywords jet*, hydrogen*, and alcohol*, according to the Web of Science [18]. In 2006, there were more than 200. In view of several available reviews on aromatic systems [19–21], the focus will be on the less-studied aliphatic alcohols, which come closer to being amphiphilic models. For solutions, where the first studies using nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy date back more than half a century, a recent review concentrating on sterical

hindrance effects is available [22]. In the solid [23], packing effects always compete with the intrinsic properties of the isolated or cooperative hydrogen bonds. While clusters are also postulated as highly fluxional units in the supercritical state [24, 25] and in solution [26], their detailed understanding rests on a proper characterization at lower temperatures. At room temperature, the cluster concentration in the vapor phase of alcohols is fairly low and thermal excitation still makes an interpretation of the spectra difficult [27]. Therefore, the present review concentrates on cold molecular aggregates, which are most conveniently produced and studied in adiabatic gas expansions or jets [28]. The ultimate goal is to use the detailed insights gained in such low-temperature gas-phase studies to better understand the hydrogen bond and conformational behavior in the liquid state [29, 30].

After raising a selection of topical issues in this field and briefly introducing some spectroscopic and numerical techniques to probe the hydrogen bond dynamics, recent results for alcohol clusters are presented in order of increasing complexity. They are followed by some general conclusions and an outlook on future research goals.

II.   ISSUES

Among the wealth of issues relevant to hydrogen bonding in alcohol clusters, this review will focus on aspects related to hydrogen bond patterns and on the dynamical implications over a wide range of time scales. Some key questions connected to these aspects will be formulated.

A.   Structures and Topologies

$O—H\cdots O$ hydrogen bonds have a strong preference for a nearly linear arrangement. Furthermore, electrostatic forces or lone electron pair considerations direct the hydrogen that is attached to the accepting oxygen into an approximately tetrahedral angle with respect to the hydrogen bond. The tetrahedral lone-pair picture has recently been debated [31], based on electron density maps and earlier structural evidence on poly-alcohols [32]. While there is certainly significant acceptor potential in the region between the two lone pairs, the two studies [31, 32] may be biased in overestimating it slightly. Pauli repulsion will have to be included in the recent study [31] and distortions due to the optimization of multiple hydrogen bonds and steric constraints in the solid state have to be considered in the earlier analysis [32]. When taken into account, both effects are likely to recover a certain tetrahedral preference in isolated hydrogen bonds. This may or may not be cast into a lone-pair picture. At least it is an extremely useful ordering principle for alcohol cluster structures, which does not rule out exceptions.

In line with this, alcohols form unsymmetric dimers with well-separated donor and acceptor roles [33] and a more or less pronounced preference for one of the acceptor lone pairs, depending on secondary interactions (see Fig. 1). For trimers, the option to form a ring with three hydrogen bonds usually wins over the hydrogen bond strain and over steric repulsion between the alkyl groups which this induces. However, the open-chain structure with two unstrained hydrogen bonds is not too far in energy and always should be considered for vibrationally excited clusters [34] and whenever secondary interactions come into play [35, 36]. Furthermore, trimer formation can be suppressed at least at elevated temperatures [37], if the alkyl chain becomes too bulky. For the tetramer, a cyclic structure involves less strain and less sterical hindrance than in the trimer and is thus particularly attractive (Fig. 1). The alkyl groups can alternate between positions above and below the hydrogen bond plane and better avoid each other, if they are too big. Again, this alternation can also be interpreted as being due to a lone-pair preference. In terms of pure repulsion, a planar arrangement of all heavy atoms is indeed competitive, if the alkyl group
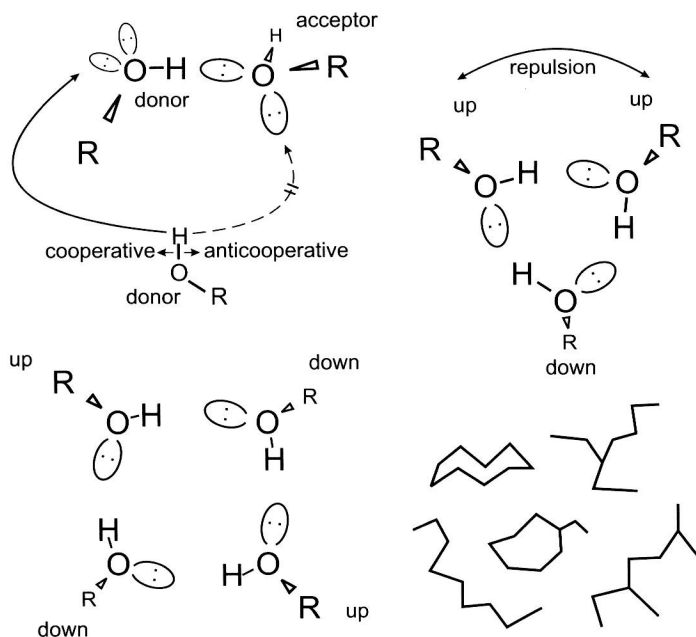

Figure 1. Illustration of lone-electron-pair preferences in alcohol dimers, cooperative and anticooperative binding sites for a third monomer, ring strain and steric repulsion in alcohol trimers, alternation of residues in alcohol tetramers, and chain, branch, and cyclic hydrogen bond topologies in larger clusters.

is not too big. Rings with homodromic hydrogen bond patterns remain energetically attractive for larger clusters [38], but the entropic advantage of chain structures, where the terminal alcohol molecules only form single strong hydrogen bonds, and branched topologies, where alcohol molecules serve as double acceptors, tends to grow. Chain topologies can reduce steric congestion by forming helical structures, whereas branching tends to be more sterically demanding. Isomerism is therefore an important issue beyond a cluster size $n = 4$ [39] and possibly even before. In the solid, infinite chains and helices are often realized for simple alcohols [40], but cyclic structures are also conceivable [41] and quite abundant for bulky species [7, 42–44]. The structure of liquid alcohols is heavily debated [45]. Entropy arguments would predict winding chains of variable length to be quite important. The missing hydrogen bond compared to cyclic clusters can be partly compensated by the polar environment and by branching points. A finite cluster model of liquid alcohols [45] will necessarily be biased toward small clusters, closed rings, and compact structures, because it cannot reproduce the dramatic increase of conformational and topological entropy in extended flexible chains and dynamical network structures. Nevertheless, a detailed characterization of small clusters can bring us closer to a structural understanding of liquid alcohols.

The basic aggregation pattern in alcohol clusters can of course be influenced in any desired direction by the design of the alkyl group, a feature that makes alcohols attractive in molecular recognition studies. Molecular additives can further modify the topological preferences. By offering a pure hydrogen bond acceptor group such as an ether, terminated chain structures can be favored over rings [46]. By adding a local or global charge, major disruptions of the ring topology are possible, because charge coordination competes with the hydrogen bond network [47, 48]. However, the fundamental preference of alcohol clusters to form hydrogen-bonded ring patterns is never lost completely and reappears whenever other constraints start to relax.

B. Energetics

Unfortunately, not many techniques allow us to probe the binding energy of a hydrogen-bonded complex directly [20, 49–51]. With very few exceptions [52, 53], they are restricted to aromatic (π-) systems, where the intrinsic strength of a single alcoholic hydrogen bond is typically superimposed [54] and may even be overwhelmed [55] by π-interactions. Therefore, one often has to rely on quantum chemical sources for energy information [56, 57]. It is essential to calibrate these techniques against the few available experimental benchmark data, such as for methanol dimer [52], phenol–methanol [20], or 1-naphthol complexes [51]. Relative energy orders of isomers are even more important [50] and can sometimes be obtained by jet relaxation studies [58]. The strength of a hydrogen bond can be influenced by introducing electron-donating and electron-withdrawing alkyl

groups. Quite naturally, the hydrogen bond donor quality increases for electronegative substituents, whereas the acceptor quality decreases. For homodimers—that is, complexes built from identical subunits—the two influences compete with each other. Furthermore, the organic substituents can undergo their own intermolecular interactions, either among themselves or with the functional units of the O—H···O hydrogen bond. Therefore, cluster binding energies are measures of the total interaction between the interacting molecules, which may or may not be dominated by a single classical hydrogen bond interaction. Donor–acceptor roles can become quite intricate in multifunctional systems [59]. This is another important motivation for studying the simplest prototype systems, where any secondary interactions are minimized.

C.   Cooperativity

Another factor that influences the aggregation pattern and energetics of alcohol clusters is cooperativity [60]. Once a molecule engages as a hydrogen bond donor, it automatically becomes a better acceptor and *vice versa* due to the polarization of the O—H bond. This favors chain-like and even more cyclic topologies over branched networks of hydrogen bonds [61]. The latter are less stable, because two or more molecules must compete for the electron density at the acceptor oxygen (Fig. 1). It is more favorable for the third molecule to extend the polarization chain of the other two, rather than to interrupt it. The prototype system for this is hydrogen fluoride [62], which, more so than the reactive OH radical [63], may serve as the topological parent compound for alcohol aggregation. Its pronounced hierarchy of interactions (strong 1-D aggregation via cooperative hydrogen bonds, weak 3-D aggregation via dispersive forces) can be systematically attenuated by increasing the size of the alkyl group. This hierarchy is responsible for cluster formation in alcohol vapor even under thermodynamic equilibrium conditions [14, 64, 65].

Although cooperative effects are sometimes invoked whenever a property (such as a hydrogen bond length) changes from the dimer to larger aggregates [66], a many-body decomposition approach can uncover non-pairwise additive effects more rigorously [67]. The natural cluster size to study cooperativity is a trimer. The total energy of a trimer E_{ABC} can be decomposed into monomer energies E_A, E_B, E_C, pair interaction terms $V_{AB} = E_{AB} - E_A - E_B$, $V_{AC} = E_{AC} - E_A - E_C$, $V_{BC} = E_{BC} - E_B - E_C$, and a three-body interaction

$$V_{ABC} = E_{ABC} - E_{AB} - E_{AC} - E_{BC} + E_A + E_B + E_C$$

such that

$$E_{ABC} = E_A + E_B + E_C + V_{AB} + V_{AC} + V_{BC} + V_{ABC}$$

Only the effects of the three-body interaction term V_{ABC} are truly cooperative effects in a trimer, although properties may of course also change with cluster size in a strictly pairwise additive model, where $V_{ABC} = 0$. The formalism may easily be extended to larger clusters and indeed three-body effects tend to be more important in larger clusters than in trimers [68].

For chain-like or cyclic hydrogen bond patterns between three alcohol molecules A, B, and C, V_{ABC} is usually negative (attractive). If molecule B acts as an acceptor for both A and C, V_{ABC} is typically repulsive (positive), because A and C compete for the electron density at B [61]. This anti-cooperativity provides the main explanation why branching of hydrogen-bonded chains is discouraged in alcohols.

D. Hydrogen Bond Isomerism and Conformational Isomerism

For the reasons outlined above, hydrogen bond isomerism in alcohols is less pronounced than it might be on statistical grounds, considering that every acceptor oxygen offers a choice between two lone electron pairs. For ring topologies, there are of course different ways of arranging the alkyl groups already in the trimer and different ways of puckering the $(-OH)_n$ ring, starting with the tetramer or pentamer. Like isomerism within the alkyl chain [69], these are conformational choices that leave the classical hydrogen bond pattern intact. Hydrogen bond isomerism is less abundant. Lasso structures [39], in which double acceptor alcohol units come into play, only become competitive when the ring strain has leveled off—that is, for $n \geq 4$. The simple reason is that any molecule that is taken out of the ring makes the cycle smaller and increases ring strain. This penalty adds to the anti-cooperative effect present in double-acceptor centers. Open-chain structures are possibly competitive in small, highly strained clusters and become asymptotically equivalent to rings for $n \to \infty$. The best way to stabilize them for intermediate cluster sizes appears to be the introduction of secondary interactions in the alkyl group. Such a secondary stabilization can be an aromatic substituent [35].

When mixed clusters of alcohols are formed, the issue of donor–acceptor isomerism comes into play [58]. Both alcohols can act as donors and acceptors, but the difference between their donor (Q_D) and acceptor (Q_A) qualities $(Q_D - Q_A)$ will not be the same. The molecule that features the smaller difference will preferentially act as an acceptor. The molecule that has the larger difference will prefer the donor position. If the roles are interchanged, the hydrogen bond strength of the complex decreases, but the structure may still represent a local minimum on the potential energy hypersurface. The determination of donor and acceptor qualities in hydrogen-bonded clusters is not straightforward. Energetic quantities such as binding energies are difficult to attribute to single interaction sites. Vibrational red shifts of the O—H stretching fundamental may be more suitable parameters to analyze the donor–acceptor

preference [58], because they closely correlate to hydrogen bond length and strength [70]. Furthermore, they are experimentally more easily accessible.

E. O—H Stretching Dynamics

The infrared (IR) spectrum provides some of the most clear-cut observables for hydrogen bonding phenomena. Alcohol clusters have been studied in most detail in the O—H stretching fundamental range. The reasons for this are both technical and scientific. Tunable IR lasers have traditionally been versatile and powerful in the 3-μm window. The effects of hydrogen bonding are also particularly pronounced in this range, as was recognized long ago [71]. Cooperativity and decreasing ring strain induce progressive bathochromic shifts with cluster size [16, 35]. The square of the O—H stretching transition dipole moment, responsible for IR activity, can be orders of magnitude larger in hydrogen-bonded clusters than in the alcohol monomer. Therefore, even in the absence of size-selectivity and sensitive laser sources, alcohol clusters can be detected and characterized by their O—H stretching signature [65].

The bathochromic shift or red shift of the O—H oscillator is a sensitive measure of hydrogen bond strength. Its accurate modeling is quite sophisticated, but simple approaches often profit from favorable error compensation [72]. Furthermore, the frequency of an O—H oscillator correlates more or less linearly with the length of the O—H bond, with a red shift of about $14 \, cm^{-1}$ for a bond length extension by $0.001 \, \text{Å}$ [63]. In larger clusters, the intrinsic red shift of the individual oscillators is superimposed by coupling effects among the originally degenerate oscillators of the individual alcohol monomers, the so-called Davydov couplings [16]. The strongest red shift is observed for concerted in-phase O—H stretching motion of all members of the hydrogen bond cycle. This is an early indicator for concerted hydrogen transfer between the molecules [73], in which the hydrogen-bonded protons switch their chemical bond partners in a cyclic way. The result is an equivalent hydrogen bond pattern running in the opposite direction. The pronounced red shift also reflects cooperativity, because a stretched O—H bond has an increased dipole moment, which enhances the intermolecular interaction.

Infrared enhancement in the O—H stretching fundamental upon hydrogen bond formation can be large, but may be smaller than predicted by traditional quantum chemistry methods [74]. There are few ways to experimentally determine absolute infrared enhancements by hydrogen bond formation [74], because the experimental number density of the clusters usually remains unknown. Instead, theoretical band strengths are often used to estimate the cluster number density [75]. The situation is more favorable if a cluster contains two or more nonequivalent O—H groups. In such a case, the intensity ratio between these groups can be determined by direct absorption methods [30, 76]. As a rule, Raman scattering cross sections are less sensitive to hydrogen bonding [16] but show similar qualitative trends.

The splitting patterns of the degenerate O—H oscillators upon cluster formation [77] can be described by a simple model, which is inspired by Hückel molecular orbital theory [16, 78]. These Davydov splittings reflect a periodic flow of energy among the coupled oscillators. For trimers, its period T is roughly related to the coupling constant W (in cm^{-1}) involved, according to

$$T \approx \frac{1}{3cW}$$

where c is the speed of light. Note that the dissipative formula for the lifetime τ

$$\tau \approx \frac{1}{2\pi cW}$$

has also been invoked in this context [78]. It agrees quite closely with the half-period of the oscillation. There are usually further, slower dissipative processes, by which the energy deposited in the O—H stretching manifold is redistributed within the alcohol molecules and into the hydrogen bond [21]. If these IVR processes are sufficiently fast and the density of coupling states is high enough, they can be detected as a contribution to the linewidth of the cluster O—H stretching band [16]. In any case, the two time–wavenumber relationships listed above are useful qualitative and semiquantitative concepts to translate spectral features into temporal evolutions of a localized wavepacket. For monomers and dimers, where the energy dissipation out of a locally excited O—H oscillator is relatively slow, IVR usually has to be detected by time-resolved experiments [21], which can provide further insights into the sequential mechanism.

The Davydov coupling constants W may be studied as a function of cluster geometry, cluster size, isotope composition, and alkyl group substitution [16]. They contain valuable information about the nature of the hydrogen bond interaction in alcohol clusters. The mechanism by which the Davydov couplings between initially degenerate O—H oscillators arises may be described in different ways. One may interpret it as a through-hydrogen-bond process, similar to classical oscillator coupling through chemical bonds. At the other end, one may interpret it as a purely through-space long-range coupling of the oscillating dipoles. Considering that hydrogen bonds between alcohols are dominated by dipole–dipole interactions, an excitonic dipole–dipole model appears to be adequate [78]. The coupling constant can then be estimated from the geometry and transition dipole moment of the cluster [78].

F. Isotope and Overtone Effects

A characteristic feature of hydride stretches in general [79] and the O—H oscillator in alcohols in particular [80] is its frequency isolation from other