Tuning the Hydrogen Bond Donor/Acceptor Isomerism in Jet-Cooled Mixed Dimers of Aliphatic Alcohols[†]

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Hydrogen bonded complexes between two different aliphatic alcohols exhibit donor/acceptor isomerism. In a supersonic jet expansion, the less stable isomer can isomerize to the more stable isomer if the energy difference is sufficiently large and the barrier sufficiently low. We show by FTIR jet spectroscopy that this is progressively the case for methanol/methanol-d_1, methanol/ethanol, and methanol/*tert*-butyl alcohol, until no metastable donor/acceptor isomer persists in the expansion. Collisional relaxation experiments, ^{18}O labeling and quantum chemical calculations are used to assign the spectra. Differences between energetical and spectroscopic acceptor strengths are discussed.

Introduction

When a hydrogen bond is formed between two aliphatic alcohols, one OH group acts as the hydrogen bond donor and the other one acts as the hydrogen bond acceptor. This leads to isomerism, whenever the two alcohols are chemically[1] or conformationally[2] different. Obviously, the most stable hydrogen bond isomer is that in which the "better" donor donates its hydrogen to the "better" acceptor, rather than vice versa. However, this apparently straightforward statement gives rise to several questions. How can one measure donor and acceptor strength? Do the results correlate with common organic chemistry rules about inductive effects? Are donor and acceptor strength trends always anticorrelated in alcohols? Can vibrational spectroscopy be used to study such isomerism? Will the less favorable isomer coexist with the more stable one in a supersonic jet expansion?[3]

Our goal is to answer some of these questions using dimers of the simplest aliphatic alcohols such as methanol (MeOH), ethanol (EtOH), and *tert*-butyl alcohol (*t*-BuOH). This makes quantum chemical predictions feasible, but it precludes the most sensitive spectroscopic techniques, such as laser-induced fluorescence or soft ionization, which require suitable UV chromophores. Direct absorption IR spectroscopy is thus the method of choice. Due to sensitivity limitations, it has so far been constrained to matrix isolation studies for these systems.[1] We have recently developed supersonic jet FTIR spectroscopy to the point where such systems can also be routinely studied in vacuum isolation.[4] An alternative approach would be cavity ringdown laser absorption spectroscopy.[5] Another alternative would be the use of microwave spectroscopy, if the high-resolution spectra can be assigned to individual conformations.[6] For smaller molecules and clusters, insightful isomerization experiments in rare gas expansions have been carried out before.[7]

In any case, the vacuum environment allows for a more direct comparison to theory, as matrix perturbations[1,8] are avoided. This is vital if the isomer effects occur on a sub-kilocalorie scale. As an example for interesting matrix perturbations, Coussan et al.[1] very recently studied mixed methanol/ethanol dimers. Methanol was found to be the donor in Ar matrices, whereas it acts as the hydrogen bond acceptor toward ethanol in an N_2 matrix. At the same time, the preferred conformation of ethanol in these matrices is inverted from trans to gauche, like in the corresponding matrix isolated monomers.[9,10] This underlines the usefulness of vacuum isolation studies for such subtle isomerizations.

The symmetry in alcohol dimers can be broken in different ways. The most subtle effects are expected for isotope substitution. While heavy atom substitution is most useful for labeling purposes,[1] deuteration can have a pronounced influence on the isomer equilibrium due to zero point energy effects. In general, deuterium prefers the bound position, where its reduced vibrational amplitude can lead to a significant lowering of the zero point energy. In contrast, energetical and spectroscopic effects of acceptor deuteration on the donor vibrations are often quite subtle.[11,12] The symmetry in an alcohol dimer can also be broken by conformational isomerism, if donor and acceptor molecules adopt different conformations, such as in ethanol dimer.[2,6,10]

Finally, chemical substitution offers a robust way to distinguish between hydrogen bond isomers. Substitution of hydrogen atoms by methyl groups in methanol, such as in the case of ethanol or *tert*-butyl alcohol, is expected to increase the acceptor strength of an OH group, whereas it might be thought to weaken the donor strength. Both effects can be attributed to the +I effect of the substituted methyl groups, which increases the electron density at the oxygen atom. As will be seen, this simple picture must be viewed with some caution.

In the present study, we move from the delicate isomerism in methanol/methanol-d_1 dimers over the large variety of isomers in the methanol/ethanol system to the more simple case of methanol/*tert*-butyl alcohol. In all cases, FTIR spectra of jet-cooled dimers were recorded, assignment is supported by isotope substitution and collisional relaxation, comparison to harmonic quantum chemical calculations is made, and implications for concepts of donor/acceptor isomerism are discussed.

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Methods

OH (OD) stretching fundamentals of alcohol dimers were obtained by ragout-jet FTIR spectroscopy[4] and its recent filet-jet variant.[13,14] Dimers were produced together with monomers and some larger clusters in a supersonic jet expansion at ≈10−20 K rotational temperature by coexpanding the alcohols at sub-percent concentrations with the carrier gas He through pulsed slit nozzles (12 cm × 0.05 cm in the ragout-jet and 60 cm × 0.02 cm in the filet-jet). A vacuum buffer of 23 m^3 volume allowed to accommodate gas pulses of typically 140 ms length at a background pressure below 1 mbar. It was further evacuated down to 0.1 mbar by a series of roots pumps within about 30 s before the next gas pulse was admitted to the buffer. Full interferometer scans of an FTIR spectrometer (Bruker, IFS 66v/S, *l*-N_2 cooled InSb detector) were synchronized to the gas pulse. The resolution of the spectra was 2 cm^{-1} if no other value is given.

The binary alcohol mixtures were prepared by bubbling He through two thermostated saturators, one for each alcohol, into a 65 L reservoir. The mixing ratio was adjusted by the saturator temperature, by a separate He flow and by pulsed admission of each gas to the reservoir via magnetic valves. The alcohol concentrations are calculated on the basis of gas-phase IR spectra of the mixtures, which are compared to gas-phase spectra of the pure alcohols. In some experiments, traces of Ar were added to the He carrier gas to enhance the cluster relaxation in the expansion. The amount of Ar in the gas mixture was determined by mass spectrometry in some cases and estimated from the gas flow in others.

Methanol (MeOH, dried, Merck), methanol-d_1 (MeOD, 99% D, Aldrich), ^{18}O methanol (Me^{18}OH, 95% ^{18}O, Campro Scientific), ethanol (EtOH, dried, Merck), *tert*-butyl alcohol (*t*-BuOH, 99%, Lancaster), He (99.996%, Messer), and Ar (99.998%, Messer) were used as supplied.

Geometry optimizations and harmonic frequency calculations were carried out using the Gaussian03[15] program suite (including earlier versions) for various basis sets and different levels of electron correlation treatment. Single-point CCSD(T) calculations were performed with the MOLPRO suite of programs.[16] To compensate in first order for anharmonic effects and deficiencies in the electronic structure treatment, all harmonic dimer OH stretching wavenumbers ω(th) were shifted by the difference between the experimental monomer wavenumber $\tilde{\nu}_M$(exp) and the harmonic monomer wavenumber prediction ω_M(th):

$$\tilde{\nu}(\mathrm{th}) = \omega(\mathrm{th}) + \tilde{\nu}_M(\mathrm{exp}) - \omega_M(\mathrm{th}) \qquad (1)$$

Donor and Acceptor Strengths and Red Shifts

Before presenting computational and spectroscopic results on mixed alcohol dimers, a brief discussion of hydrogen bond donor and acceptor strength and possible spectroscopic observables is adequate.

Four hydrogen bonded dimers AA, BB, AB, and BA can be constructed from the two alcohol monomers A and B, where the first letter in the dimer refers to the donor and the second to the acceptor. Let AB be more stable than BA and let D(AB) be the dissociation energy of AB into its fragments A and B. Thus, we choose the convention:

$$D(\mathrm{AB}) - D(\mathrm{BA}) > 0 \qquad (2)$$

A measure for the donor strength of A relative to B (D_{AB}) would be

$$D_{AB} = \frac{(D(\mathrm{AB}) - D(\mathrm{BB})) + (D(\mathrm{AA}) - D(\mathrm{BA}))}{2} \qquad (3)$$

It is the average energy gain when B is replaced by A as a donor in one of the four dimers.

The corresponding measure for the acceptor strength of A relative to B (A_{AB}) would be

$$A_{AB} = \frac{(D(\mathrm{AA}) - D(\mathrm{AB})) + (D(\mathrm{BA}) - D(\mathrm{BB}))}{2} \qquad (4)$$

It is the average energy gain when B is replaced by A as an acceptor in one of the four dimers.

The isomer difference $\Delta E_D = D(\mathrm{AB}) - D(\mathrm{BA})$, which is of interest in the present context, is thus simply given by

$$\Delta E_D = D(\mathrm{AB}) - D(\mathrm{BA}) = D_{AB} - A_{AB} \qquad (5)$$

Therefore, AB is more stable than BA if the relative donor strength of A exceeds the relative acceptor strength of A. D_{AB} and A_{AB} need not have opposite signs (i.e., the better donor does not have to be the poorer acceptor)!

This is best illustrated with one of the very few examples, where experimental dissociation energies are largely available for a set of four dimers, namely, HF/DF.[17] We identify A with DF, as FD···FH is clearly more stable than FH···FD due to zero point energy reduction in the hydrogen bond librations. Thus, $D(\mathrm{AB}) \approx 13.84$ kJ/mol,[18−20] $D(\mathrm{BA}) \approx 12.94$ kJ/mol,[19,20] $D(\mathrm{AA}) \approx 14.06$ kJ/mol,[21] and $D(\mathrm{BB}) \approx 12.70$ kJ/mol.[17,22] The relative donor strength of A is D_{AB}/(kJ/mol) = (1.14 + 1.12)/2 = 1.13. The relative acceptor strength of A is A_{AB}/(kJ/mol) = (0.22 + 0.24)/2 = 0.23. DF is both a better donor and a better acceptor than HF, but its donor superiority exceeds its acceptor superiority and thus FD···FH is more stable than FH···FD.

Spectroscopically, a similar analysis can be carried out by considering the hydrogen bond induced red shifts of X−H stretching fundamentals. For the same donor, these red shifts somehow reflect the acceptor strength of the hydrogen bond partner, whereas the donor strength would have to be probed by an acceptor vibration. The sensitivity of hydrogen bond induced red shifts provides an excellent spectroscopic probe of the acceptor strength, while suitable donor strength probes will be more difficult to find. Thus, one can define a quantity

$$A_{AB}^{\mathrm{spec}} = -\frac{(\tilde{\nu}(\mathrm{AA}) - \tilde{\nu}(\mathrm{AB})) + (\tilde{\nu}(\mathrm{BA}) - \tilde{\nu}(\mathrm{BB}))}{2} \qquad (6)$$

based on donor fundamental wavenumbers ($\tilde{\nu}$) as a local spectroscopic probe of hydrogen bond acceptor strength, which may or may not correlate with the energetical quantity (A_{AB}) from eq 4. The minus sign results from the low-frequency shift of donor vibrations upon hydrogen bond formation.

For the well-studied HF/DF system, $\tilde{\nu}(\mathrm{AA}) = 2834.62$ cm^{-1},[23] $\tilde{\nu}(\mathrm{AB}) = 2838.05$ cm^{-1},[19] $\tilde{\nu}(\mathrm{BA}) = 3867.72$ cm^{-1},[19] and $\tilde{\nu}(\mathrm{BB}) = 3868.31$ cm^{-1}.[23] According to eq 6, $A_{AB}^{\mathrm{spec}}/\mathrm{cm}^{-1} = 2.01$, consistent with DF being a slightly better acceptor than HF. This is in line with the energetical finding and provides some validation for the proposed approach.

Correlations between binding energies and hydrogen bond induced red shifts[24−27] have been proposed and refined ever since the linear Badger−Bauer relationship was postulated in 1937.[28] The present analysis concentrates on aspects of donor/acceptor interchange and does not rely on the validity of energy/

TABLE 1: Dissociation Energies (in kJ/mol) of Alcohol Dimers in the Notation Donor + Acceptor with (D_0) and without (D_e) Harmonic Zero Point Energy Correction Calculated at MP2 (in parentheses B3LYP) Level for a range of basis sets: (A) 6-31+G(d), (B) 6-311++G(d,p), (C) 6-311++G(2d,p), and (D) 6-311++G(3df,2p)[a]

	A		B		C		D	
dimer	D_e	D_0	D_e	D_0	D_e	D_0	D_e	$D_{e,c}$
MeOH + MeOH	32.1	25.5	28.5	22.4	26.8	21.2	−	−
	(26.0)	(19.7)	(24.4)	(18.6)	(−)	(−)	[−]	[−]
MeOD + MeOD	32.1	−	28.5	23.4	26.8	22.1	−	−
	(26.0)	(20.7)	(24.4)	(19.5)	(−)	(−)	[−]	[−]
t-BuOH + *t*-BuOH	40.3	34.4	35.5	−	−	−	−	−
	(23.9)	(17.9)	(21.6)	(16.4)	(−)	(−)	[−]	[−]
MeOH + MeOD	32.1	−	28.5	22.5	26.8	21.4	−	−
	(26.0)	(19.9)	(24.4)	(18.8)	(−)	(−)	[−]	[−]
MeOD + MeOH	32.1	−	28.5	23.2	26.8	22.0	−	−
	(26.0)	(20.5)	(24.4)	(19.4)	(−)	(−)	[−]	[−]
MeOH + $EtOH_t$	−	−	−	−	29.2	23.0	28.6	24.4
	(26.5)	(20.3)	(−)	(−)	(−)	(−)	[28.3]	[25.4]
$EtOH_t$ + MeOH	−	−	−	−	26.6	21.4	25.6	21.9
	(25.4)	(19.6)	(−)	(−)	(−)	(−)	[25.6]	[23.1]
MeOH + $EtOH_g$	−	−	−	−	29.9	24.1	29.2	24.9
	(26.8)	(20.4)	(−)	(−)	(−)	(−)	[28.8]	[25.9]
$EtOH_g$ + MeOH	−	−	−	−	26.2	20.6	27.2	23.2
	(25.1)	(18.8)	(−)	(−)	(−)	(−)	[26.9]	[24.2]
MeOH + *t*-BuOH	37.3	30.7	32.9	−	−	−	−	−
	(27.2)	(20.9)	(24.9)	(19.5)	(−)	(−)	[−]	[−]
t-BuOH + MeOH	34.1	28.0	30.7	−	−	−	−	−
	(23.5)	(17.3)	(21.8)	(16.1)	(−)	(−)	[−]	[−]

[a] The entry in brackets under (D) is an energy calculation at the CCSD(T)/avtz' level[2] at the same geometry. All other values are obtained after geometry optimization. $D_{e,c}$ is the dissociation energy after counterpoise correction.[39] The dissociation of dimers containing ethanol is relative to the monomer fragments.

TABLE 2: Relative Donor ($D_{MeOD-MeOH}$) and Acceptor Strength ($A_{MeOD-MeOH}$) of MeOD in MeOH/MeOD (in kJ/mol) Calculated at Harmonic B3LYP and MP2 Level for Basis Sets A to C from Table 1[a]

method	basis set	$D_{MeOD-MeOH}$	$A_{MeOD-MeOH}$	$\Delta E_{0,D}$	ΔE_S	$\Delta E_{0,S}$
B3LYP	A	0.8	0.2	0.6	5.9	4.6
	B	0.75	0.15	0.6		
MP2	B	0.85	0.15	0.7	7.0	5.5
	C	0.75	0.15	0.6		

[a] Also given is the difference in zero point energy levels ($\Delta E_{0,D}$) and the electronic interconversion barrier (ΔE_S) as well as the barrier from the excited isomer to the ground state isomer ($\Delta E_{0,S}$).

red-shift correlations. It actually points out limits of such correlations, as will be seen below.

Results and Discussion

MeOH/MeOD. The most elementary mixed aliphatic alcohol dimer system is that of methanol with methanol-d_1. In the absence of zero point energy, both mixed isomers are of course energetically equivalent within the Born−Oppenheimer approximation. In analogy to HF, one expects MeOD to engage preferentially as a donor because of the reduced zero point energy destabilization of the librational modes.[29] This is confirmed by simple harmonic calculations, which are summarized in Table 1. The corresponding relative donor and acceptor strengths of MeOD are given in Table 2. MeOD is a better hydrogen bond donor, and to a lesser degree also a better hydrogen bond acceptor than MeOH.

Whether both mixed MeOH/MeOD dimers are formed in a supersonic jet expansion depends on the energy difference between the two and on the barrier height for the donor/acceptor exchange. For the predicted energy difference of about 0.6 kJ/mol, one would expect almost complete conversion to the most stable dimer at a final supersonic jet temperature of about 10−20 K. However, the equilibrium between isomers is typically frozen at much higher temperatures in earlier stages of the expansion. Therefore, the energy barrier for isomer interconversion is decisive. For methanol dimer, the corresponding first-order saddle point involves a planar arrangement of the two OH groups. The OOH angle is close to 47−48°, and the imaginary wavenumber amounts to 50−60 cm^{-1}. The electronic barrier for interconversion is 6−7 kJ/mol. Including zero point energy, this is lowered to about 5 kJ/mol from the excited-state perspective (see Table 2). This barrier heigth may be just enough to stabilize the metastable isomer with MeOD in the hydrogen bond acceptor role under supersonic jet conditions.

It remains to be discussed whether the mixed dimers can be distinguished spectroscopically from their homodimer counterparts. The donor OH (OD) stretching chromophore is fairly localized and may not be shifted sufficiently in frequency upon deuteration of the acceptor OH. Harmonically, the predicted shift is indeed very small, on the order of 0.1−0.3 cm^{-1} and quite independent of the employed level of theory. Its sign is such that acceptor deuteration leads to a slight red shift for the MeOD donor and to a slight blue shift for the MeOH donor. These purely harmonic mass effects are likely to be overlapped by larger anharmonic contributions, which affect the acceptor strength via effective bond elongation and distortion due to zero point motion. Indeed, the energetical data in Table 2 suggest that MeOD is the better acceptor. From this, one expects a red shift upon acceptor deuteration, which is at variance with the purely harmonic mass effect for the MeOH donor.

At this stage, the experimental ragout-jet FTIR spectrum of mixed MeOH/MeOD expansions in He can be discussed. Figure 1 compares the region of the OH stretch vibration for isotopically mixed (trace (b)) and pure MeOH (trace (a), scaled to match the dimer band intensity) expansions. The mixing ratio in trace (b) is about MeOH:MeOD = 1:2. The methanol monomer absorption (M) peaks at 3686 cm^{-1} (see Table 3) in accordance with ref 4. It also includes any OH stretching bands of pure acceptor molecules, in particular from the dimer. At lower wavenumber the donor bands of dimers (D), trimers (T), and tetramers (Te) occur. The vibrational bands have overlap-

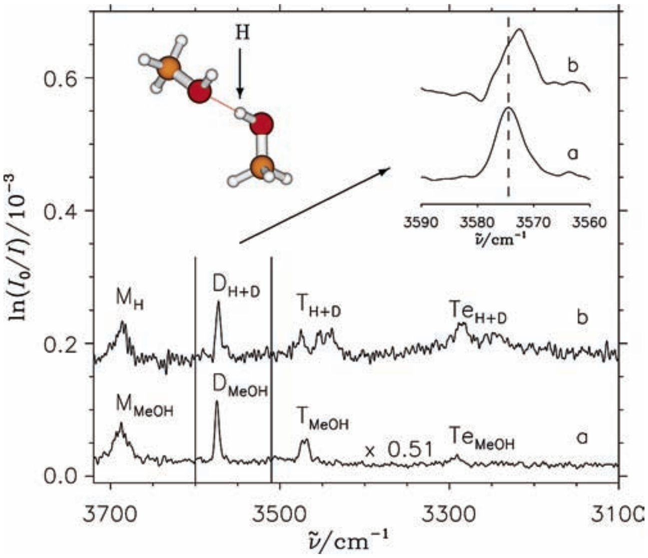


Figure 1. Jet spectra of MeOH/MeOD in He in the region of the OH stretch vibration. Trace (a) shows pure MeOH ($c_{\mathrm{MeOH}} \simeq 0.6\%$), and trace (b) shows a mixture ($c_{\mathrm{MeOH}} \simeq 0.3\%$, $c_{\mathrm{MeOD}} \simeq 0.6\%$). The dashed line marks the band position of the MeOH homodimer. See text for further explanations.

TABLE 3: Experimental $\tilde{\nu}$(exp) and Corrected Harmonic $\tilde{\nu}$(th) Wavenumbers at Different Levels of Theory (in cm^{-1}) of the OH Stretch Vibration of Methanol Monomers and Dimers

$\tilde{\nu}$(exp)	$\tilde{\nu}$(th)(B3LYP/A)	$\tilde{\nu}$(th)(B3LYP/B)	$\tilde{\nu}$(th)(MP2/C)	assignment
3686	3686	3686	3686	MeOH
3575	3543	3533	3534	$(\mathrm{MeOH})_2$
3573	3543	3533	3534	MeOH···MeOD
2718	2718	2718	2718	MeOD
2638	2615	2608	2608	MeOD···MeOH
2637	2615	2608	2608	$(\mathrm{MeOD})_2$

ping contributions from OH stretching motions in partially deuterated and nondeuterated clusters. This is indicated in the notation (index H + D). The trimer bands show a significant isotope effect. Its analysis is beyond the scope of the present article, but it may shed some light onto the controversial interpretation of the methanol trimer spectrum.[4,30−32] The change in the dimer band is more subtle. Therefore the region from 3590 to 3560 cm^{-1} is displayed as an enlarged inset in Figure 1. The band position of the MeOH dimer at 3575 cm^{-1} is marked with a dashed line. This shows that the absorption peak in the mixture is red-shifted by about 2 cm^{-1}. Due to MeOH dimer band overlap, the real band position of the mixed dimer may be somewhat lower than 3573 cm^{-1}. Its accurate determination by subtraction of the MeOH dimer part is not trivial due to the unknown partition of D among the three possible isotopomers. However, the mere existence of the isotope shift proves that the metastable mixed dimer is indeed present in the expansion.

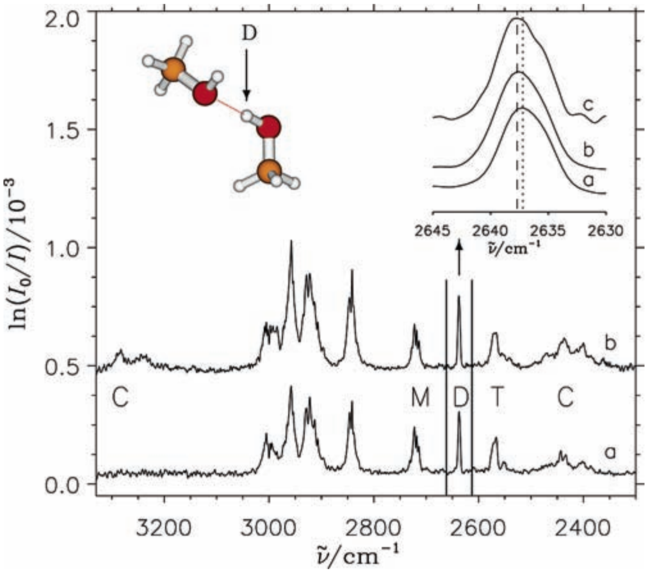


Figure 2. Jet spectra of MeOH/MeOD in He in the region of the OD stretch vibration. Trace (a) shows pure MeOD, and trace (b) shows a mixture ($c_{\mathrm{MeOH}} \simeq 0.4\%$, $c_{\mathrm{MeOD}} \simeq 0.8\%$). Spectrum (c) has a resolution of 1 cm^{-1}. The band position of the MeOD homodimer is marked with a dotted line, and the approximate position of the MeOD···MeOH dimer is marked with a dashed line.

Ragout-jet FTIR spectra of the OD stretch region are shown in Figure 2. Trace (a) is the spectrum of pure MeOD, and trace (b) is obtained from the mixture. The capital letters refer to both spectra and label the monomer (M), dimers (D), trimers (T), and higher clusters (C). The CH stretch vibrations are located between 3040 and 2830 cm^{-1}. C bands around 3250 cm^{-1} are due to OH stretching modes in partially deuterated clusters and do not occur in spectrum (b), supporting its isotopic purity. The change in the dimer band between trace (a) and trace (b) is even more subtle than in the OH stretch region. Again the dimer region is enlarged in an inset. The band position of the MeOD homodimer is marked with a dotted line to emphasize the slight shift toward higher wavenumber upon MeOH addition. Trace (c) is the original 1 cm^{-1} resolution version of trace (b), which has 2 cm^{-1} resolution, like trace (a). A low frequency shoulder is common to all spectra. From the slight spectral shift, it can be concluded that the mixed MeOD···MeOH dimer is shifted by about 0.5 cm^{-1} to the blue of the MeOD homodimer. This shift is four times smaller than that of MeOH···MeOD relative to $(\mathrm{MeOH})_2$, but in line with the expectation of a better relative acceptor strength of MeOD.

The experimental wavenumbers for monomers and dimers are summarized in Table 3 and compared to harmonic predictions that were adjusted to the monomer band center according to eq 1. Apart from the failure to predict the subtle acceptor deuteration shifts, one may note the consistent overestimation of the dimer red shifts at B3LYP and MP2 level.[33,34] Isotope-substituted methanol has previously been investigated by matrix isolation techniques.[11,12] IR spectra in the region of the OH stretch vibration of MeOH-d_3 and a mixture of MeOH-d_3 with MeOD-d_3 showed shifts of the OH donor in the mixed dimer below 0.5 cm^{-1}, qualitatively consistent with our findings, if matrix effects are considered.

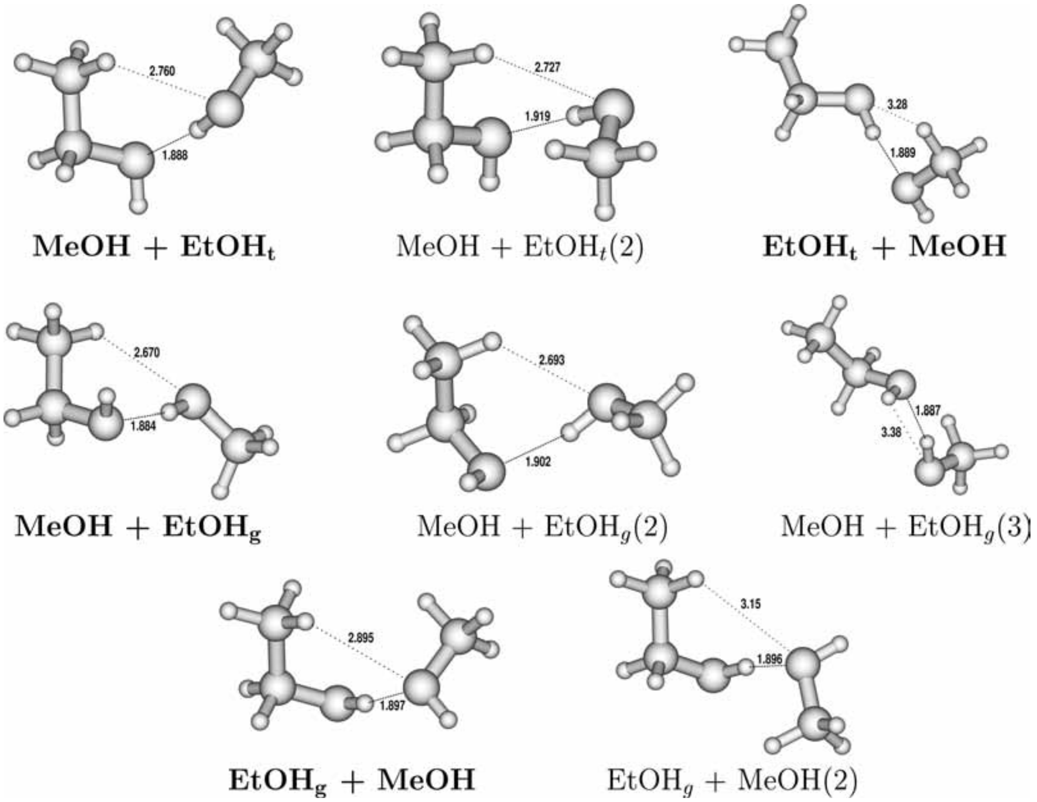
In summary, MeOH/MeOD is a system where the relaxation in the supersonic He jet remains incomplete. A barrier of about 5 kJ/mol is thought to be responsible for the survival of the metastable mixed dimer, in which MeOH acts as a hydrogen bond donor toward MeOD. Spectroscopic and energetical acceptor strengths are consistent with each other.

MeOH/EtOH. The mixed dimer of methanol and ethanol is an elementary example in which conformational, donor/acceptor[1] and diastereomeric isomerism occur at the same time. Ethanol exists in a trans (*t*, also called anti) and in two enantiomeric gauche conformations (*g*+, *g*−) with very subtle energy balance.[2] Starting with the *t* conformation and looking along the O → C bond vector in a Newman projection, *g*+ is the conformation in which the O−H bond is rotated clockwise by 120°. When ethanol engages in a hydrogen bond with methanol as the donor or as the acceptor, a new asymmetric center emerges at the acceptor oxygen atom. In a simplistic view, there is a choice between two oxygen lone pairs. Looking again

TABLE 4: MeOH/EtOH Dimers in Four Different Isomer Classes Together with Relative Energies (in kJ/mol) at MP2 Level with Basis Set D, with (ΔE_{CP}) and without (ΔE) Counterpoise Correction[a]

donor + acceptor	type	ΔE_{CP}	ΔE	$r_{\mathrm{O\cdots H}}$/pm	$\Delta E_{\mathrm{CP}}^{\mathrm{CCSD(T)}}$	$\Delta E^{\mathrm{CCSD(T)}}$
MeOH + EtOH$_t$	compact	**0.0**	**0.0**	276	0.0	0.0
MeOH + EtOH$_t$ (2)	compact	1.8	1.6	273		
EtOH$_t$ + MeOH	open	**2.4**	**3.0**	328	2.4	2.7
MeOH + EtOH$_g$	compact	**0.3**	**0.3**	267	0.2	0.1
MeOH + EtOH$_g$ (2)	compact	2.3	2.6	269		
MeOH + EtOH$_g$ (3)	open	2.6	2.9	338		
EtOH$_g$ + MeOH	compact	**1.9**	**2.3**	290	1.9	2.0
EtOH$_g$ + MeOH (2)	open	2.6	3.2	315		

[a] Compact $g+-$ethanol structures involve the right acceptor oxygen lone pair. The shortest intermolecular O−C−H distance $r_{\mathrm{O\cdots H}}$ (in pm) is also given. The most stable isomers of each class that are considered in the spectral analysis are marked in bold face. For them, relative CCSD(T) energies with ($\Delta E_{\mathrm{CP}}^{\mathrm{CCSD(T)}}$) and without ($\Delta E^{\mathrm{CCSD(T)}}$) counterpoise correction (in kJ/mol) are also given.



MeOH + EtOH$_{\mathrm{t}}$ MeOH + EtOH$_t$(2) **EtOH$_{\mathrm{t}}$ + MeOH**

MeOH + EtOH$_{\mathrm{g}}$ MeOH + EtOH$_g$(2) MeOH + EtOH$_g$(3)

EtOH$_{\mathrm{g}}$ + MeOH EtOH$_g$ + MeOH(2)

Figure 3. Mixed MeOH/EtOH dimer structures calculated at the MP2/6-311++G(3df,2p) level of theory. The hydrogen bond length and the shortest secondary oxygen contact for each isomer are given in Å. See also Table 4.

along the O → C bond vector, we denote the lone pair in clockwise direction from the O−H bond as the right lone pair. Together with the donor/acceptor isomerism, this leads to 3 × 2 × 2 isomers in a rotational isomeric state picture, which form 6 pairs of enantiomers. A recent study[1] investigated four of these structures. On the other hand, a systematic search on the potential energy hypersurface shows that there are multiple minima for some of the six rotational isomers that arise from secondary interactions with C−H groups.[35] The combination of left lone pair and $g+$ conformation (or by mirror symmetry also right lone pair and $g-$ conformation) at the ethanol acceptor generally leads to more open structures than left-$g-$ (or right-$g+$) combinations. The compactness of the latter appears to provide a slight energy advantage via interactions of the methyl group in ethanol with the oxygen in methanol, as seen in Table 4 and Figure 3. According to harmonic calculations at lower level, this qualitative conclusion is not changed by the addition of zero point energy.

Based on the energetics in Table 4, one expects at least two isomers in the jet in which MeOH acts as a donor and EtOH$_{g/t}$ as an acceptor. They are very close in energy. It is not clear whether the trans or the gauche isomer is more stable, as the monomer gauche/trans energy difference is off by 0.5 kJ/mol at MP2 level for this large basis set[2] and zero-point energy effects are not included (see however Table 1).

The reverse isomers with ethanol as the hydrogen bond donor compete energetically with higher-lying MeOH···EtOH isomers. In most cases, these higher-lying isomers are only minima on the potential energy hypersurface. With the inclusion of zero point energy, the barriers of the corresponding rearrangement reactions tend to vanish. Therefore, the lowest isomers of each class are highlighted in the table as the most likely candidates for spectral assignment. Computed dissociation energies of these four mixed MeOH/EtOH dimers for a range of basis sets and methods with and without zero point energy correction, D_0 and D_e, are compared to those of other dimers in Table 1. They are in line with those obtained at B3LYP/6-311++G(2d,2p) level.[1] One should note that the dissociation values in Table 1 refer to monomer fragments in the relevant conformation; therefore, the dimers involving gauche EtOH have a stronger binding energy,

TABLE 5: Barrier Heights of the Donor/Acceptor Exchange Motion in MeOH/EtOH and MeOH/*t*-BuOH Dimers at B3LYP/6-31+G(d) Level[a]

	ΔE_D	ΔE_S	$\Delta E_{0,D}$	$\Delta E_{0,S}$	$\tilde{\nu}_i$	δ	γ
MeOH/EtOH$_t$	0.9	5.7	0.6	4.7	−48	47.7 (46.0)	177.9
MeOH/EtOH$_g$	1.7	5.2	1.6	3.9	−48	48.3 (45.2)	179.2
MeOH/*t*-BuOH	3.8	4.4	3.6	3.1	−42	49.1 (44.9)	172.1

[a] ΔE_D ($\Delta E_{0,D}$) is the energy difference between the *AB* and *BA* dimer without (with) zero point energy (in kJ/mol). The energy difference ΔE_S ($\Delta E_{0,S}$) between the saddle point and the less stable isomer is also given. $\tilde{\nu}_i$ is the imaginary wavenumber of the saddle point (in cm^{-1}). The geometry at the saddle point is described by the HOO-angle δ of the donor (acceptor) and the HOOH-dihedral angle γ (in deg).

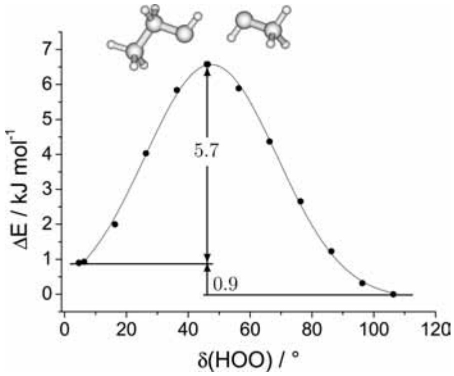


Figure 4. Potential energy of the MeOH/EtOH$_t$ dimer along the HOO-angle δ calculated at the B3LYP/6-31+G* level of theory.

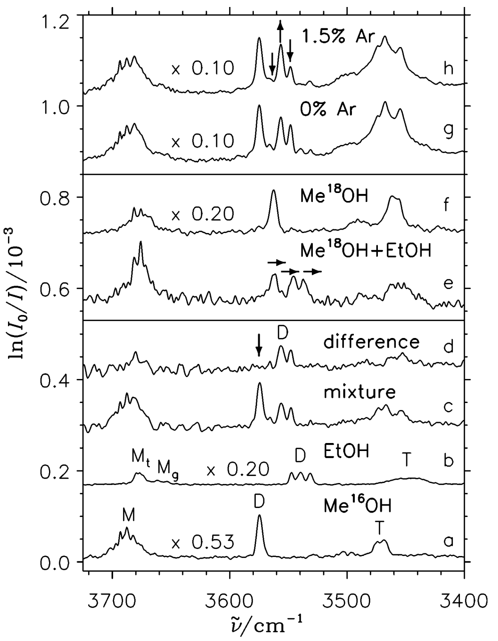


Figure 5. (Traces a−d) Ragout-jet FTIR spectra of methanol ($c_{\mathrm{MeOH}} \simeq 0.06\%$), ethanol ($c_{\mathrm{EtOH}} \simeq 0.04\%$) and the mixed expansion of methanol/ethanol in He. ($c_{\mathrm{MeOH}} \simeq 0.02\%$, $c_{\mathrm{EtOH}} \simeq 0.008\%$). (Traces e and f) Ragout-jet FTIR spectra of Me^{18}OH (e) without ($c_{\mathrm{MeOH}} \simeq 0.25\%$) and (f) with EtOH added ($c_{\mathrm{MeOH}} \simeq 0.04\%$, $c_{\mathrm{EtOH}} \simeq 0.02\%$). (Traces g and h) Filet-jet FTIR spectra of the mixed expansion of methanol and ethanol (g) without and (h) with ≃ 1.5% Ar addition. Scaling factors applied to individual spectra are given as "× 0.nm".

although in absolute terms they may be energetically higher in energy than those involving trans EtOH (see Table 4). The subtle monomer isomerization energy renders an analysis of the relative donor and acceptor strengths of ethanol and methanol less useful at the present stage than for MeOH/*t*-BuOH (see next section).

Whether the less stable isomers with methanol as hydrogen bond acceptor persist in a supersonic jet is crucially dependent on the barrier for interconversion into the more stable MeOH···EtOH isomers. This is analyzed in Table 5. As for MeOH/MeOD, the exchange is mainly a motion along the HOO coordinate. The barrier can be located in a one-dimensional scan along this coordinate. Figure 4 shows such a scan for the MeOH/EtOH$_t$ dimer at the B3LYP/6-31+G(d) level. The angle δ between the OH bond of the donor or the acceptor and the O···O vector is again close to 45° at the barrier. The exact barrier was located by using the highest point of the scan as a starting point for a transition state optimization (opt = TS) implemented in Gaussian.[15] Its first-order saddle point character was verified by a force field calculation. In contrast to MeOH/MeOD, the HOOH dihedral angle deviates slightly from 180°. The electronic barrier height as viewed from the less stable isomer is 5.7 kJ/mol. If the zero point energy of n vibrations at the local minimum and of all $n - 1$ true vibrations at the saddle point are added, the barrier is reduced to 4.7 kJ/mol. On the basis of the similar energetics in MeOH/MeOD, one may expect that some dimers in the jet expansion are stabilized in the less stable donor/acceptor arrangement. However, one should not dismiss other routes for interconversion, involving a third molecule. While such dimer−molecule collisions are more than 3 orders of magnitude less frequent than dimer−rare gas collisions in our diluted experiment, they may be more efficient in terms of donor/acceptor interconversion.

These calculations set the stage for the spectroscopic study of mixed MeOH/EtOH expansions. Its results are summarized in Figure 5. Traces (a) and (b) show ragout-jet FTIR spectra of pure methanol[4] and ethanol[2] in the OH stretch region. Monomers, dimers, and trimers are marked with M (trans and gauche in the case of ethanol), D, and T. Here, we concentrate on the dimer region. The donor OH stretch vibrations of ethanol dimer occur at 3547, 3539, and 3531 cm^{-1}, red-shifted with respect to the single methanol dimer band at 3575 cm^{-1}. We could recently show that the lowest wavenumber band contains the most stable dimer conformation, a homoconfigurational gauche form.[2] Trace (c) provides the ragout-jet FTIR spectrum of a mixed expansion. The concentration of ethanol is only about half that of the methanol to avoid overlapping ethanol dimer bands. Apart from the strong methanol dimer band, only the ethanol dimer band at 3531 cm^{-1} due to the most stable ethanol dimer survives. This may be a result of the enhanced collisional relaxation by the added methanol. Three new bands occur at 3567, 3556, and 3548 cm^{-1} (i.e., just between the bands of the pure dimers). The most blue-shifted band carries only about one-fifth of the intensity of the other bands and overlaps with the wing of the methanol dimer band. After scaling and subtraction of the methanol dimer band via trace (a), the difference spectrum (d) is obtained. It clearly exhibits the three bands attributed to mixed dimers.

Identification of the donor molecule in these mixed dimers is possible by the use of Me^{18}OH,[1] as shown in trace (e). The heavier frame shifts the OH stretching modes to lower frequencies. This is seen for the monomer, but also for the three dimer peaks in trace (c). The most blue-shifted peak is due to MeOH dimer, as evidenced by a pure Me^{18}OH expansion shown in trace (f). It is red-shifted by 13 cm^{-1} relative to Me^{16}OH. This value agrees well with the predicted shift of 12 cm^{-1} calculated at the B3LYP/6-31+G(d) level of theory and also with the change in the square root of the reduced mass of an isolated OH oscillator. The other two dimer peaks at 3546 and 3537 cm^{-1} in trace (e) form the same pattern as in trace (c), merely shifted by 10−11 cm^{-1}. Thus, both of them can be assigned to mixed dimers with methanol in the donor position. For the third

TABLE 6: Experimental $\tilde{\nu}$(exp) and Monomer Corrected Harmonic Wavenumbers $\tilde{\nu}$(th) of the OH Stretch Vibrations of MeOH/EtOH Dimers (in cm^{-1})[a]

donor + acceptor	$\tilde{\nu}$(th)	$\tilde{\nu}$(exp)	experimental assignment
$EtOH_t$ + MeOH	3526	3567?	secondary minimum
$EtOH_g$ + MeOH	3522	3567?	secondary minimum
MeOH + $EtOH_t$	3520	3556	MeOH donor, global minimum
MeOH + $EtOH_g$	3513	3548	MeOH donor, secondary minimum

[a] The harmonic wavenumbers have been calculated at MP2 level using the 6-311++G(2d,p) basis set.

and weakest mixed dimer band, no such statement is possible. A shift of at least two MeOH stretching bands by 11 cm^{-1} upon ^{18}O-isotope substitution is also observed in an Ar matrix.[1] It would be consistent with a plausible matrix red shift of 30−40 cm^{-1}.

Additional information about the energy sequence of the conformers can be obtained through enhancement of the collisional relaxation in the expansion. This is achieved by the admixture of Ar to the He expansion and has been applied successfully in the related cases of ethanol dimers[2] and 2-fluoroethanol dimers.[36] For this purpose, we use small amounts of Ar to minimize condensation on the molecular clusters, which would result in red shifts and broadening. Trace (g) shows a filet-jet spectrum of MeOH/EtOH in pure He and trace (h) the same spectrum with 1.5% Ar added. Note the increased absorbance (scaling factor 0.1) in the filet-jet spectra due to the longer path length and higher concentration for the same clustering ratio, as compared to the ragout-jet FTIR spectrum in trace (c).[13,37] Ar reduces the intensity of the most red-shifted band at 3548 cm^{-1} and increases the intensity of the band at 3556 cm^{-1}, without changing their width or position. This is strong evidence for an assignment of the 3556 cm^{-1} band to the most stable mixed dimer. The weak mixed dimer band at 3567 cm^{-1} and the central ethanol dimer band at 3539 cm^{-1} are also attenuated by Ar addition, emphasizing that they belong to metastable dimer conformations.

Under our experimental conditions, Ar condensation on the dimers to form nanomatrices[2] was avoided. In this context, the bulk matrix work of Coussan et al.[1] should be discussed. It also used ^{16}O/^{18}O substitution for the donor/acceptor identification. In an Ar matrix, methanol was found to act as a donor toward trans ethanol, whereas in an N_2 matrix the inverse pairing is favored and ethanol adopts the gauche conformation. This underlines the influence of matrix perturbations on subtle hydrogen bond isomerism and calls for an accurate modeling of the matrix environment.[8]

Table 6 shows the experimental wavenumbers and their Ar-relaxation and ^{18}O assignment in comparison with harmonic wavenumbers for the lowest structures of each isomer class. The harmonic wavenumbers have been calculated at MP2 level using the 6-311++G(2d,p) basis set and individually monomer corrected according to eq 1. The two strong bands correlate well with the two most red-shifted harmonic predictions, if a uniform shift by 35 cm^{-1} is allowed for. Such a shift is in good agreement with harmonic calculations carried out for several conformations of the ethanol dimer.[2] There, the shift amounted to ≈33 cm^{-1} at the same level of theory and was attributed mostly to torsional zero-point motion, which reduces the anharmonicity in the dimer. This validates the assignment put forward in ref 2 for ethanol dimer. Anharmonic corrections based on conventional second-order perturbation theory were also carried out at MP2/6-31++G(2d,p) level. They are sizable, but differ by at most 3 cm^{-1} among the four investigated MeOH/EtOH dimers and thus do not affect our conclusions.

TABLE 7: Relative Donor ($D_{MeOH-tBuOH}$) and Acceptor Strengths ($A_{MeOH-tBuOH}$) of MeOH in MeOH/*t*-BuOH (in kJ/mol) Calculated at Harmonic MP2 and B3LYP Level for Basis Sets A and B[a]

method	basis set	$D_{MeOH-tBuOH}$	$A_{MeOH-tBuOH}$	$\Delta E_{0,D}$	$A^{spec}_{MeOH-tBuOH}$
B3LYP	A	2.7	−0.9	3.6	−20
	B	2.8	−0.6	3.4	−22
MP2	A	−3.1	−5.8	2.7	−36

[a] Also given is the difference in zero point energy levels ($\Delta E_{0,D}$) and the calculated spectroscopic acceptor strength ($A^{spec}_{MeOH-tBuOH}$) (in cm^{-1}) based on harmonic OH stretching wavenumbers.

Beyond the uniform 35 cm^{-1} shift of the calculated wavenumbers, the agreement between theory and experiment is astonishing and to some degree fortuitous. The most red-shifted band is consistently assigned to a MeOH donor isomer, which represents a secondary minimum, possibly involving a gauche ethanol conformation. The strongest mixed dimer band is consistently assigned to the global minimum structure, again featuring a MeOH donor. Energy and wavenumber predictions suggest that it involves a trans ethanol conformation, although by a very small margin. Thus, the trans conformational preference of ethanol monomer appears to be preserved in MeOH/EtOH dimers, whereas it is changed to gauche in ethanol dimer.[2] An experimental MeOH stretch splitting between the gauche and trans ethanol conformations of 6 cm^{-1} is to be compared to the calculated value of 8 cm^{-1}. This is well within expected error bars, which would also allow for an interchange of the two bands. In the matrix isolation study,[1] at least two MeOH stretching bands of mixed dimers were also observed, but no evidence for a gauche ethanol conformation was found. All together, the detailed conformational assignment of these two bands must remain tentative. Our results confirm that Ar relaxation studies are able to differentiate between nearly isoenergetic conformations, still beyond the absolute accuracy of state of the art quantum chemical predictions.

The assignment of the weakest and most blue-shifted MeOH/EtOH band at 3567 cm^{-1} must also remain uncertain. It may well be due to an inverted conformation with MeOH as the hydrogen bond acceptor, but assignment to a secondary MeOH···EtOH minimum from Table 4 cannot be ruled out completely despite shallow interconversion barriers. Thus, it remains open whether the MeOH/EtOH system is fully relaxed to the most stable donor/acceptor sequence in supersonic He expansions or whether both hydrogen bond isomers are present. In any case, the slight (0.5 kJ/mol) trans conformational preference of ethanol monomer is nearly neutralized in its complexes with methanol donor. This also seems to be the case for phenol/ethanol dimers,[38] where experiment showed the trans ethanol conformation to be slightly more stable than the gauche conformation.

MeOH/*t*-BuOH. As the MeOH/EtOH-pair is borderline in terms of the quenching of the less stable donor/acceptor isomer, it is appropriate to extend the investigation to MeOH/*t*-BuOH. Here, the donor preference for methanol should be more pronounced. In addition, torsional isomerism is absent in *tert*-butyl alcohol, which renders the spectral interpretation more straightforward.

Table 1 shows dissociation energies (D_e, D_0) (in kJ/mol) for MeOH/*t*-BuOH dimers calculated at the B3LYP and MP2 levels of theory with the basis sets 6-31+G(d) and 6-311++G(d,p). As expected, the dissociation energies depend strongly on the level of theory at these low levels. It is instructive to dwell on the relative donor and acceptor strengths in this case (Table 7).

The energy difference between the two mixed dimers is fairly robust. The mixed dimer with methanol as the donor is about

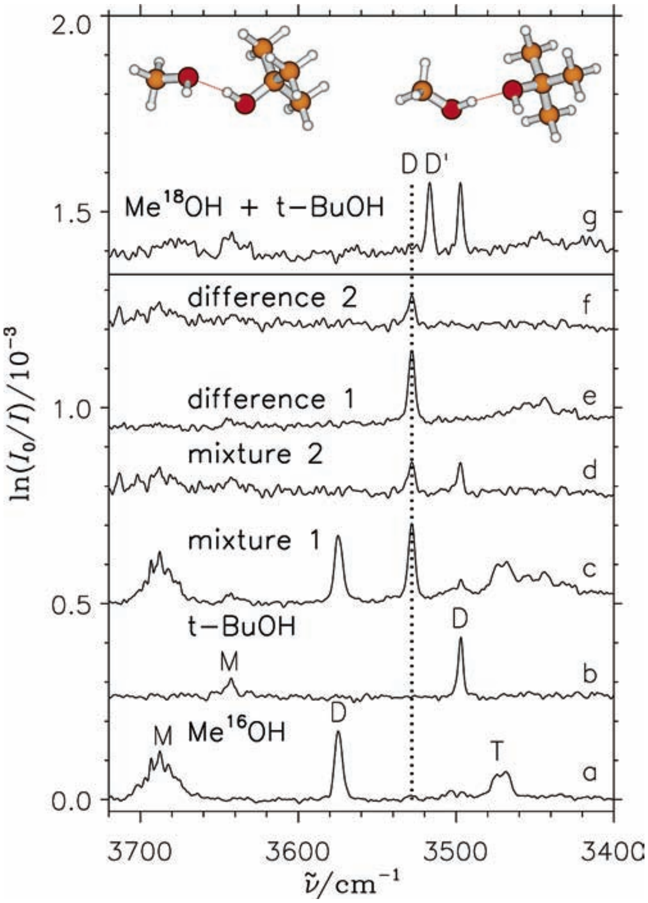


Figure 6. OH stretching spectra of MeOH/*t*-BuOH jet expansions in He. The band position of the mixed dimer is marked with a dotted line. The concentrations of the pure alcohols are $c_{\mathrm{MeOH}} \simeq 0.06\%$ (a) and $c_{t-\mathrm{BuOH}} \simeq 0.02\%$ (b). In mixture (c), the MeOH concentration ($c_{\mathrm{MeOH}} \simeq 0.24\%$) is an order of magnitude higher than the concentration of *t*-BuOH ($c_{t-\mathrm{BuOH}} \simeq 0.02\%$). In mixture (d), the concentrations are similar ($c_{\mathrm{MeOH}} \simeq c_{t-\mathrm{BuOH}} \simeq 0.03\%$). The difference spectra (e and f) are obtained as (e) = (c) − 0.14 × (b) − (a) and (f) = (d) − 0.18 × (b). The concentrations in spectrum (g) are $c_{\mathrm{Me^{18}OH}} \simeq 0.07\%$ and $c_{t-\mathrm{BuOH}} \simeq 0.02\%$.

2−4 kJ/mol more stable than the dimer with *tert*-butyl alcohol as the donor. This is more than in the previously discussed examples of MeOH/MeOD and MeOH/EtOH. The relative donor and acceptor strengths, whose difference yields the desired isomerization energy, are strongly dependent on the method. At B3LYP level, methanol is the better donor (positive sign of $D_{\mathrm{MeOH-tBuOH}}$) and *tert*-butyl alcohol is the better acceptor (negative sign of $A_{\mathrm{MeOH-tBuOH}}$), as one might have expected. At MP2 level, *tert*-butyl alcohol is by far the better acceptor but also becomes the better donor. This difference may be due to basis set superposition error (BSSE), which is larger at the MP2 level for such a small basis set or due to dispersion interactions, which are poorly described at B3LYP level. It is inherent in the corresponding homodimers. Thus, *t*-BuOH dimer is more stable than MeOH dimer at MP2/6-31+G(d) level, whereas the opposite is true at the corresponding B3LYP level. This issue has already been discussed before.[34] Larger basis set calculations will have to show which factor dominates. Preliminary results for related systems indicate that the inadequate description of dispersion interactions at B3LYP level is dominant. We anticipate that this deficiency of the B3LYP approach will become more and more obvious when larger systems are addressed. However, the present analysis already illustrates that energetical measures of donor and acceptor strengths are intrinsically nonlocal and susceptible to interactions beyond the hydrogen bond itself. Toward a small molecule, a large molecule will always tend to be a good donor *and* acceptor due to its dispersion interactions with the smaller molecule.

In contrast to the intrinsically nonlocal energetics, hydrogen-bond induced donor red shifts may be expected to reflect more of the local hydrogen bond acceptor strength. This is supported by the calculated values in Table 7, which are consistently negative for methanol relative to *tert*-butyl alcohol. Thus, one expects a mixed MeOH donor dimer which is red-shifted with respect to methanol dimer and a less stable mixed *t*-BuOH donor dimer whose hydrogen-bonded OH stretch is blue-shifted with respect to *t*-BuOH dimer.

In a more general context, the above analysis indicates fundamental limits for any correlation between dimerization energy and hydrogen bond induced red shift. The fact that such correlations work surprisingly well[25] may be related to the fact that most of the measurements are carried out in solution. There, nonspecific dispersion interactions may be balanced by the solvent, such that red shift and binding energy parallel each other. In the gas phase, where nondirectional cohesion forces add to directional hydrogen bonds, such correlations may be more limited.

The interconversion between donor−acceptor isomers is facilitated by the predicted large energy difference of about 3 kJ/mol between the two isomers. Results at B3LYP/A level are summarized in Table 5. The barrier has a zero point energy corrected height of only 3.1 kJ/mol for the metastable isomer and involves a nonplanar HOOH torsional angle. In extension of the circumstantial evidence for metastable isomers in the higher barrier case of MeOH/EtOH, only one mixed MeOH/*t*-BuOH isomer is expected in the jet expansion.

The ragout-jet FTIR spectra of MeOH and *t*-BuOH (see also ref 34) in He in the spectral range of the OH stretch vibration are shown in Figure 6(a and b). The spectrum of the mixed expansion (c) contains a new band at 3529 cm^{-1}, which is located between the band of the MeOH dimer at 3575 cm^{-1} and the band of the *t*-BuOH dimer at 3497 cm^{-1}. It is therefore assigned to a mixed dimer. This is confirmed by the difference spectrum (e). In spectrum (c), the concentration of MeOH is about 10 times higher than the concentration of *t*-BuOH. This results in mixed trimers which overlap with the *t*-BuOH dimer band. Reduction of the MeOH concentration by a factor of 10 leads to spectrum (d). Only the *t*-BuOH dimer band and the

TABLE 8: MeOH/*t*-BuOH Monomer (M), Dimer (D) and Trimer (T) OH Stretching Wavenumbers (in cm^{-1}) from Experimental (exp) and Various Levels of Monomer Corrected Harmonic Predictions

$\tilde{\nu}$(exp)	$\tilde{\nu}$(B3LYP/A)	$\tilde{\nu}$(B3LYP/B)	$\tilde{\nu}$(MP2/A)	*t*-BuOH	MeOH	donor + acceptor
3686	3686	3686	3686		M	
3643	3643	3643	3643	M		
3575	3543	3533	3568		D	
3529	3520	3510	3536			MeOH + *t*-BuOH
-	3516	3503	3541			*t*-BuOH + MeOH
3497	3499	3483	3508	D		
3471	-	-	-		T	

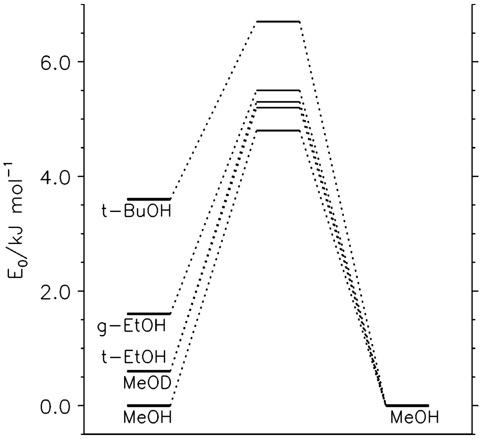


Figure 7. Donor/acceptor isomerization of MeOH, MeOD, EtOH$_g$, EtOH$_t$, and *t*-BuOH in a dimer with methanol. Shown are the zero point energy corrected B3LYP/6-31+G(d) levels (labeled by the donor molecule) and the corresponding transition states, linked by dotted lines.

band of the mixed dimer persist, leading to a clean difference spectrum (f). The profile of the mixed dimer band is narrow and shows no sign of band overlap under both expansion conditions.

Experimental and monomer corrected harmonic wavenumbers of the OH stretch vibration are listed in Table 8. B3LYP fails to describe the MeOH dimer shift whereas the MP2/A small basis set prediction is reasonable, as discussed before.[34] The predictions for *t*-BuOH dimer are closer to experiment. The two mixed dimers are predicted at wavenumbers between those of the pure dimers, separated by only 4−7 cm^{-1}. Their sequence varies with the level of theory. Thus, a unique assignment of the single experimental band at 3529 cm^{-1} to one or even both of the mixed dimers is not possible based on the red shift alone. The energetics suggests that the band is either due to the dimer with MeOH as the donor or—less likely—due to a fortuitous overlap of two mixed dimer absorptions.

To exclude the latter possibility, trace (g) of Figure 6 shows the ragout-jet spectrum of a mixture of *t*-BuOH and Me^{18}OH. As in trace (d), only the band of the *t*-BuOH dimer and the single band of a mixed dimer (D′) at 3517 cm^{-1} can be seen. It is 12 cm^{-1} red-shifted as compared to the position of the mixed dimer band (D) in spectrum (e). The latter band has disappeared completely. This shows unambiguously that the observed mixed dimer has methanol in the donor role and that the excited dimer with *t*-BuOH as the donor is not formed in the expansion. The barrier of about 3 kJ/mol appears to be surmountable under He slit jet expansion conditions.

Conclusions

When two alcohols form a mixed hydrogen bonded dimer, one of the two donor/acceptor isomers will be energetically preferred, but the other one may still be stabilized in a supersonic jet expansion, if the energy difference is sufficiently small and the interconversion barrier sufficiently high. We show how the energy difference between the two isomers can be decomposed into relative donor strength and acceptor strength contributions, which are not necessarily complementary to each other. We use the IR hydrogen bond donor OH stretching shift as a spectroscopic measure of acceptor strength, which appears to be more local in nature than the corresponding energetical quantity.

From MeOH/MeOD over MeOH/EtOH$_{g/t}$ to MeOH/*t*-BuOH, the energy difference between the two donor/acceptor isomers increases about 5-fold, whereas the barrier from the metastable to the stable isomer decreases by about one-third at B3LYP level. Figure 7 shows the evolution of these quantities. While the absolute barrier heights may change with increasing level of theory, the trend should be robust. Along the series, we observe an increasingly complete isomerization of the metastable donor/acceptor combination to the stable one in supersonic He expansions. Although a more complex dimer isomerization mechanism with active participation of a third alcohol molecule cannot be ruled out, the results are consistent with a “unimolecular” mechanism in a bath of random collisions.

The quantum chemical results for MeOH/EtOH dimers are able to describe the energetics and spectroscopy of the ethanol torsional isomerism. They validate our earlier conclusions about the preferred homoconfigurational structure of ethanol dimer.[2]

Collisionally induced relaxation experiments and isotope substitution prove to be useful tools in jet FTIR spectroscopy. Three key experiments for MeOH clusters, MeOH/EtOH dimers and MeOH/*t*-BuOH dimers carried out with all together less than 1 g of Me^{18}OH underline that ragout-jet FTIR spectroscopy—despite its use of molar gas pulses—is a highly sensitive and powerful technique to probe the dynamics of hydrogen bonded clusters.

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