UvA-DARE (Digital Academic Repository)

Hydrogen bonding in acidic zeolites observed by time-resolved vibrational spectroscopy

Brugmans, M.J.P.; Kleyn, A.W.; Lagendijk, A.; Jacobs, W.P.J.H.; van Santen, R.A.

DOI

[10.1016/0009-2614\(93\)E1334-D](https://doi.org/10.1016/0009-2614(93)E1334-D)

Publication date

1994

Document Version

Final published version

Published in

Chemical Physics Letters

[Link to publication](#)

Citation for published version (APA):

Brugmans, M. J. P., Kleyn, A. W., Lagendijk, A., Jacobs, W. P. J. H., & van Santen, R. A. (1994). Hydrogen bonding in acidic zeolites observed by time-resolved vibrational spectroscopy. *Chemical Physics Letters*, 217(1-2), 117-122. [https://doi.org/10.1016/0009-2614\(93\)E1334-D](https://doi.org/10.1016/0009-2614(93)E1334-D)

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

Hydrogen bonding in acidic zeolites observed by time-resolved vibrational spectroscopy

Marco J.P. Brugmans, Aart W. Kleyn, Ad Lagendijk

FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

Wim P.J.H. Jacobs and Rutger A. van Santen

Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received 9 July 1993; in final form 8 November 1993

With time-resolved vibrational spectroscopy new information is obtained about the structural environment and vibrational dynamics of acidic hydroxyls in proton loaded zeolites. From O–H vibrational population lifetimes of zeolite Y we conclude that part of the protons are hydrogen bonded. Furthermore we find that the vibrational dynamics of the O–H oscillators are influenced by a resonant coupling mechanism.

1. Introduction

Solid acids, like hydrogen exchanged zeolites, are widely applied as hydrocarbon conversion catalysts in the petrochemical industry [1]. The protons that are covalently bonded to bridging oxygen atoms in the structure form acidic Brønsted sites. The dynamical physical and chemical interactions of the protons with the zeolitic lattice are of interest in understanding the catalytic properties of these sites. We have studied the relaxation of vibrationally excited O–H groups in several zeolites with picosecond infrared saturation spectroscopy [2,3].

Previously, Casassa et al. [4] reported a vibrational relaxation experiment on O–H in zeolite ZSM-5. In that experiment the zeolite was saturated with CCl_4 which might have influenced the vibrational dynamics. Excited population lifetimes of O–H in a zeolite Y and in a mordenite were presented recently [5]. We show that from an extensive study on vibrational population lifetimes of O–H in different zeolites new information can be obtained about the interactions of the hydroxyls with the proton loaded zeolitic framework.

With conventional infrared spectroscopy two O–H stretch absorption bands are observed for zeolite

Y. We present the first conclusive evidence that the protons in the low-frequency (LF) band are hydrogen bonded to other lattice oxygen atoms, while those in the high-frequency (HF) band are not. Furthermore we find that the vibrational lifetimes decrease with increasing proton concentration, and that this is caused by a (nearly) resonant deactivation mechanism like dipole–dipole coupling.

2. Zeolite Y

The highly symmetric structure of zeolite Y is depicted schematically in fig. 1 (see also ref. [6]). When silicon is substituted by aluminum, charge compensation is needed, and this is provided by Na^+ cations in the interstices of the structure. Proton loaded zeolites were obtained by heating in vacuo (at least 1 h at 723 K) zeolites in which (part of) the Na^+ cations were exchanged by NH_4^+ cations. All T sites ($\text{T}=\text{Si}$ or Al) in zeolite Y are crystallographically equivalent, so there are at most four different oxygen atoms around an aluminum atom to which in principle a proton can be covalently bonded, as is indicated in the smaller pictures in fig. 1. We have studied proton loaded zeolites Y with silicon to

Fig. 1. Schematic representation of the faujasite structure of zeolite Y. The corners denote the positions of the T atoms ($T = \text{Si}$ or Al), and the lines represent the bridging oxygen atoms. For clarity the hidden lines are not shown (see ref. [6] for a more extensive picture). The small pictures show the 4 different positions of the protons that are covalently bonded to the oxygen atoms around an aluminum atom ($\bullet$). The Na^+ cations (if present) are located in the cavities of the structure.

Fig. 2. Conventional room temperature infrared absorption spectra of three zeolites Y, ($\cdots$) HY/0.27, ($---$) (Na) HY/0.22, ($—$) NaHY/0.07. Two distinct peaks arising from acidic hydroxyl groups at high frequency (HF) and at low frequency (LF) are observed.

aluminum ratios of $\text{Si}/\text{Al} = 2.4$ and 2.8 and various degrees of Na^+/H^+ exchange. The samples used in the experiments presented in this Letter were self-supported discs of 3.5 to $6 \text{ mg}/\text{cm}^2$ [7,8].

The conventional room-temperature infrared absorption spectra around the O–H stretch frequency were obtained with Fourier-transform infrared spectroscopy [7,8]. Absorption spectra for three of the zeolites Y we studied are shown in fig. 2. The spectra show three distinct peaks near 3550 , 3640 and 3745 cm^{-1} , respectively (the exact absorption peak po-

sitions and widths are denoted in table 1). The absorption band at 3745 cm^{-1} is assigned to a silanol group ($=\text{Si}-\text{OH}$) at the external surface of the zeolite particle, the other bands arise from the internal acidic hydroxyl groups ($=\text{Si}-\text{OH}-\text{Al}=\text{}$) [9]. The low-frequency band is attributed to protons on O_3 and O_2 , whereas the HF band arises from protons on O_1 [9,10]. The NH_4^+ ions are more easily introduced into the supercages which leads to different relative intensities of LF and HF absorption bands for zeolites with different degrees of exchange.

3. Time-resolved experiments

We have measured O–H vibrational population relaxation times T_1 for both LF and HF absorption bands of zeolites Y (samples at room temperature), using intense picosecond tunable infrared pulses [11,12]. A 20 ps infrared pulse, typically $220 \mu\text{J}$ and wavelength tunable in the O–H absorption region, is split into a strong (99%) pump pulse and a weak (1%) probe pulse that are both focused onto the same spot on the sample (the experimental setup was described previously [12]). The pump pulse excites a significant fraction ($\approx 10\%$) of the O–H oscillators to the first excited vibrational level ($\nu = 1$) thereby bleaching the sample for the laser frequency because less oscillators are available for absorption. The decay of the pump-induced transparency, which reflects the decay of the excited population difference between $\nu = 1$ and $\nu = 0$, is probed by monitoring the transmitted probe intensity as a function of time-delay with respect to the pump pulse. The energy relaxation time T_1 can be deduced from this decay: $\ln[T(t)/T_0] \approx \exp(-t/T_1)$, where $T(t)$ is the transmitted energy of the probe pulse at delay t and T_0 is the transmitted probe energy in absence of the pump pulse. In fig. 3 the results of typical pump-probe experiments are shown for the LF and HF absorption bands of zeolites NaHY/0.07 and HY/0.27 (the number in the sample identifiers indicates the ratio of hydrogen to T atoms). Note that the LF population lifetimes are significantly smaller than the HF lifetimes and that in zeolite HY/0.27 the O–H stretch vibrations relax faster than in NaHY/0.07.

From the results of an extensive study on both zeolites, summarized in table 1, it is inferred that the

Table 1

Maxima and linewidths of O–H absorption bands and corresponding vibrational lifetimes (samples at room temperature) ^{a)}

Zeolite	Si/Al	Band	$\tilde{\nu}_{\max}$ (cm ⁻¹)	$\Delta\tilde{\nu}$ ^{b)} (cm ⁻¹)	T_1 ^{c)} (ps)	T_1/T_1^{ref}
NaHY/0.07	2.8	LF	3558	81	105 ± 18	2.58 ± 0.44
		HF	3645	19	296 ± 13	1.29 ± 0.06
(Na)HY/0.22	2.4	LF	3548	57	42 ± 8	1.16 ± 0.22
		HF	3646	16	223 ± 23	1.03 ± 0.11
HY/0.27	2.8	LF	3549	53	35 ± 4	1.00 ± 0.11
		HF	3637	24	198 ± 16	0.97 ± 0.08

^{a)} Kubota et al. reported lifetimes of $T_1^{\text{LF}} = 63 \pm 14$ ps and $T_1^{\text{HF}} = 180 \pm 12$ ps for a proton loaded zeolite Y with Si/Al = 5.6 [5].^{b)} Full width at half maximum of the absorption bands (fig. 2).^{c)} The errors in T_1 represent sample to sample variations obtained from several experiments.

population lifetimes T_1 are much longer than expected from the absorption linewidths. A lifetime of 100 ps corresponds to a bandwidth of 0.05 cm⁻¹, so the much larger absorption linewidths observed in fig. 2 (see also table 1) are not determined by T_1 , but rather by dephasing and/or inhomogeneous broadening. Therefore vibrational lifetimes of zeolites cannot be measured in the frequency domain but must be determined by time-resolved measurements.

Scanning the laser frequency through the LF absorption band we found that T_1^{LF} increases with frequency, as shown in fig. 4. Although the large laser bandwidth (34 cm⁻¹ full width at half maximum at 3600 cm⁻¹) means that the observed relaxation times are convolutions of T_1 times at frequencies within the laser bandwidth, a strong dependence is observed. No frequency dependence was found for T_1^{HF} .

4. Hydrogen bonding

The shorter vibrational lifetimes of the LF protons with respect to the HF protons (table 1) cannot be explained by relaxation to different vibrational modes. Vibrational relaxation of an O–H oscillator in a dense medium occurs by coupling to accepting modes for which the sum of the energies is in resonance with the O–H vibration. The process with the smallest number of accepting modes dominates the relaxation rate [13,14]. All oxygen atoms bridge the T atoms in zeolite Y in a very similar way (they can only be distinguished by looking at the larger cavity

structures, see fig. 1), so the nearby bonding structure is almost identical for all O atoms. In addition, the frequency difference between LF and HF absorption peaks (≈ 100 cm⁻¹) is small compared to both the frequencies of the accepting modes (≈ 1000 cm⁻¹ [7,15,16]) and the width of the compound density of states at the O–H frequency that arises from the broad accepting modes. Hence the LF and HF vibrations couple to very similar accepting modes and nearly identical T_1 lifetimes would be expected.

We propose that the difference between T_1^{LF} and T_1^{HF} must be explained by hydrogen bonding of the LF protons in zeolite Y. Hydrogen bonding of the O–H oscillator, which decreases the O–H frequency [17], increases the coupling to the accepting modes and thus decreases the vibrational lifetime [13,14]. In crystalline micas a similar decrease in O–H vibrational lifetimes was found for absorption bands that were shifted to lower frequency (equivalent to our LF peak) due to hydrogen bonding [18]. For zeolites the coupling strengths are not known, so our experiments call for a theory to make a quantitative comparison of vibrational lifetimes possible.

In addition to T_1^{LF} being shorter than T_1^{HF} , the shorter lifetimes are found at the lower frequencies within the LF absorption band (fig. 4). This is what one expects for the more strongly H-bonded O–H oscillators and is analogous to a similar observation in fused silica [19]. A stronger H bond weakens the original O–H bond more and as a consequence the frequency of that bond will be shifted to a lower frequency, while at the same time T_1 will be shorter due to a larger coupling. Thus by scanning the laser fre-

Fig. 3. Relative transmission of an infrared probe pulse $\ln(T/T_0)$ (T_0 is the transmitted probe energy in absence of the pump pulse) as function of the delay between pump and probe pulses for zeolite NaHY/0.07 (upper panel) and HY/0.27 (lower panel), for the laser frequency tuned to the maxima of the LF and the HF absorption bands. The values for the fitted energy decay times T_1 (and the corresponding standard deviations) and ν laser are for the upper panel: (●) $\nu_{\text{laser}} = 3643 \text{ cm}^{-1}$, $T_1 = 289(6) \text{ ps}$, (○) $\nu_{\text{laser}} = 3560 \text{ cm}^{-1}$, $T_1 = 124(9) \text{ ps}$; for the lower panel: (●) $\nu_{\text{laser}} = 3637 \text{ cm}^{-1}$, $T_1 = 201(2) \text{ ps}$, (○) $\nu_{\text{laser}} = 3549 \text{ cm}^{-1}$, $T_1 = 36(1) \text{ ps}$.

quency in the pump-probe experiments from low to high frequency through the LF absorption band (fig. 4), O-H vibrations with a weaker H bonding are probed sequentially. Irrespective of the exact cause of the inhomogeneous broadening, which may originate from local variations in the strength of the H bonds due to different distributions of aluminum atoms near the H bond, the frequency dependence of T_1^{LF} (fig. 4) provides decisive experimental proof for H bonding.

Although hydrogen bonding for the LF protons in zeolite Y has been suggested before [20,21], no conclusive evidence was found [9,10]. H bonding ex-

Fig. 4. Frequency dependence of T_1 when the laser is scanned over the LF absorption bands (fig. 2) for the three zeolites (×) NaHY/0.07, (□) (Na)HY/0.22, (●) HY/0.27. The x axis denotes the detuning of the top of the laser band from the maximum of the LF absorption band. The error bars represent sample to sample variations.

plains why, while having a smaller O-H stretch frequency, the LF protons are less acid than the HF protons [20,22]. It is also in agreement with the larger O-H distances for the LF hydroxyls [9] and with the presence of two close oxygen neighbours at $2.6 \text{ \AA}$ for the LF protons [9,23]. For the zeolite mordenite (Si/Al=7), which has a single absorption band around 3610 cm^{-1} [24,25], we found a similar frequency dependent T_1 around 110 ps, which suggests hydrogen bonding in this zeolite as well.

5. Resonant coupling

The (absolute) T_1 lifetimes in table 1 suggest a dependence on the proton concentration, but might be due to differences in absorbed energy densities. Experiments with varying exciting laser powers and repetition rates (normally 10 Hz) showed that considerable heating in the laser focus due to many laser pulses affects the vibrational lifetimes. Increases in temperature up to 250 K in the laser focus were estimated [26]. To be able to compare vibrational lifetimes at different proton concentrations, we measured both T_1^{LF} and T_1^{HF} for zeolite HY/0.27 as function of absorbed pulse energy density. These dependences now provide a reference lifetime T_1^{ref} at every absorbed energy density. The lifetimes in table

Table 2

Absolute and relative O–H vibrational lifetimes for deuterated versions of zeolite HY/0.27 ^{a)}

Zeolite	D/H+D ^{b)}	Band	T_1 (ps)	T_1/T_1^{ref}
HY/0.27	0	LF	35 ± 4	1.00 ± 0.11
		HF	198 ± 16	0.97 ± 0.08
DHY/0.15	0.45 ± 0.05	LF	45 ± 8	1.25 ± 0.22
		HF	273 ± 27	1.24 ± 0.12
DHY/0.05	0.81 ± 0.05	LF	59 ± 9	1.53 ± 0.23
		HF	358 ± 32	1.42 ± 0.13

^{a)} The protons were exchanged by deuterons by keeping the proton loaded zeolite samples for several hours at 700 K in D₂ gas.

^{b)} Relative concentration of deuterons as obtained from O–H and O–D stretch absorption intensities.

1 are scaled by these reference lifetimes, so that the resulting values T_1/T_1^{ref} do not depend on laser-induced temperature increases and can be compared directly.

After correction for laser heating, the T_1 lifetimes of NaHY/0.07, which has the lowest proton concentration, are still significantly longer than the T_1 of HY/0.27 (table 1). To check whether this is caused either by changes in chemical bonds or by a (nearly) resonant coupling mechanism between O–H oscillators, we decreased the proton concentration in zeolite HY/0.27 by partial deuteration. To correct for laser heating effects, the T_1 lifetimes again are scaled by lifetimes of the undeuterated zeolite at the same absorbed energy density (T_1^{ref}). As can be seen in table 2 the O–H vibrational lifetimes increase upon the introduction of O–D oscillators. Since deuteration hardly affects the accepting modes [27] nor the chemical bonds, the shorter lifetimes of zeolite HY/0.27 as compared to NaHY/0.07 must be due to a (nearly) resonant deactivation mechanism like dipole–dipole coupling. This deactivation is reduced when part of the O–H oscillators ($\approx 3600 \text{ cm}^{-1}$) is replaced by O–D oscillators ($\approx 2600 \text{ cm}^{-1}$). A more extensive study on deuterated zeolites including a discussion of the resonant coupling mechanism is in progress [26].

Acknowledgement

We would like to thank J.H.M.C. van Wolput, A.

Bot, and M.P. van Albada for fruitful discussions, and E.J. Kossen for technical assistance. The work described in this paper is part of the research program of the Stichting Fundamenteel Onderzoek van de Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Research).

References

- [1] J.M. Thomas, *Sci. Am.* April (1992) 82.
- [2] A. Laubereau and W. Kaiser, *Rev. Mod. Phys.* 50 (1978) 607.
- [3] E.J. Heilweil, M.P. Casassa, R.R. Cavanagh and J.C. Stephenson, *Annu. Rev. Phys. Chem.* 40 (1989) 143.
- [4] M.P. Casassa, E.J. Heilweil, J.C. Stephenson and R.R. Cavanagh, *J. Electron Spectry. Relat. Phenom.* 38 (1986) 257.
- [5] J. Kubota, M. Furuki, Y. Goto, J. Kondo, A. Wada, K. Domen and C. Hirose, *Chem. Phys. Letters* 204 (1993) 273.
- [6] W.M. Meier and D.J. Olson, *Atlas of zeolite structure types* (Butterworths, London, 1987).
- [7] W.P.J.H. Jacobs, J.H.M.C. van Wolput and R.A. van Santen, *Zeolites* 12 (1992) 315.
- [8] W.P.J.H. Jacobs, J.H.M.C. van Wolput and R.A. van Santen, *Zeolites* 13 (1993) 170.
- [9] M. Czjzek, H. Jobic, A.N. Fitch and T. Vogt, *J. Phys. Chem.* 96 (1992) 1535.
- [10] P.A. Jacobs and J.B. Uytterhoeven, *J. Chem. Soc. Faraday Trans. I* 69 (1973) 359.
- [11] A. Seilmeier, K. Spanner, A. Laubereau and W. Kaiser, *Optics Commun.* 24 (1978) 237.
- [12] H.J. Bakker, P.C.M. Planken, L. Kuipers and A. Lagendijk, *J. Chem. Phys.* 94 (1991) 1730.
- [13] A. Nitzan and J. Jortner, *Mol. Phys.* 25 (1973) 713.
- [14] A. Nitzan and J. Jortner, *J. Chem. Phys.* 60 (1974) 3929.
- [15] A.J.M. de Man and R.A. van Santen, *Zeolites* 12 (1992) 269.
- [16] H. Jobic, *J. Catal.* 131 (1991) 289.
- [17] D. Hadži and S. Bratos, in: *The hydrogen bond*, Vol. 2, eds. P. Schuster, G. Zundel and C. Sandorfy (North-Holland, Amsterdam, 1976) p. 565.
- [18] E.J. Heilweil, *Chem. Phys. Letters* 129 (1986) 48.
- [19] E.J. Heilweil, M.P. Casassa, R.R. Cavanagh and J.C. Stephenson, *Chem. Phys. Letters* 117 (1985) 185.
- [20] T.R. Hughes and H.M. White, *J. Chem. Phys.* 71 (1967) 2192.
- [21] L.M. Kustov, V.Y. Borovkov and V.B. Kazansky, *J. Catal.* 72 (1981) 149.
- [22] J. Hoffman, B. Hunger, U. Streller, Th. Stock, D. Dombrowski and A. Barth, *Zeolites* 5 (1985) 31.
- [23] H. Jobic, private communication.

- [24] A.K. Gosh and G. Curthoys, J. Chem. Soc. Faraday Trans. I 80 (1984) 99.
- [25] I. Bankós, J. Valyon, G.I. Kapastin, D. Kalló, A.L. Klyachko and T.R. Brueva, Zeolites 8 (1988) 189.
- [26] M.J.P. Brugmans, A.W. Kleyn, A. Lagendijk, W.P.J.H. Jacobs and R.A. van Santen, to be published.
- [27] W.P.J.H. Jacobs, J.H.M.C. van Wolput and R.A. van Santen, Chem. Phys. Letters 210 (1993) 32.