

Re-Examination of Band Deconvolution of the $\nu(\text{OH})$ Bands Observed for Bare and N_2 -Adsorbed H-mordenite

By

Fumitaka WAKABAYASHI*

Department of Science and Engineering, National Science Museum,
3-23-1 Hyakunin-cho, Shinjuku-ku, Tokyo 169, Japan

and

Junko N. KONDO, Kazunari DOMEN and Chiaki HIROSE

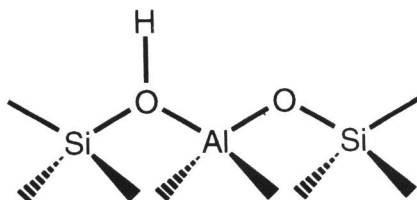
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Abstract

N_2 adsorption on H-mordenite at 110 K gives two characteristic $\nu(\text{NN})$ bands at 2335 and 2352 cm^{-1} accompanied by the drastic change of the $\nu(\text{OH})$ bands as reported in the previous work (F. WAKABAYASHI *et al.*, 1993, *J. Phys. Chem.*, **97**, 10761). Band deconvolution of the $\nu(\text{OH})$ bands observed for the bare and N_2 -adsorbed H-mordenite at 110 K is re-examined to obtain better curve-fitting than that reported previously. Considering the effect of the band shape on the deconvolution, the best curve fitting of the acidic OH band at 3616 cm^{-1} is obtained when the band is deconvoluted to a Gaussian shaped band at 3618 cm^{-1} and a Lorentzian band at 3600 cm^{-1} . Using this result, the $\nu(\text{OH})$ bands observed for the N_2 -adsorbed H-mordenite at 110 K are deconvoluted into a Gaussian band 3618 cm^{-1} , a Lorentzian band at 3600 cm^{-1} , and a Gaussian band at 3510 cm^{-1} . The decrease of the $\nu(\text{OH})$ band at 3618 cm^{-1} and the increase of the $\nu(\text{OH})$ band at 3510 cm^{-1} are linearly correlated with the increase of the $\nu(\text{NN})$ band at 2335 cm^{-1} , which clearly shows the formation of 1:1 hydrogen-bonded complex between acidic OH groups of H-mordenite and the N_2 species that gives the $\nu(\text{NN})$ band at 2335 cm^{-1} .

1. Introduction

Zeolites are microcrystalline aluminosilicate with nano-sized porous structures. Owing to their specific microstructures, zeolites have various characteristics as adsorbents and catalysts. Further, H-form zeolites have strong acidities and serve as useful solid-acid catalysts. Their acidities are classified into Brønsted acidity and Lewis acidity. The origin of Brønsted acidity has been attributed to the bridging OH groups that have a structure as follows:



In that sense, the interaction between OH groups of H-form zeolites and gas molecules is interesting from the catalytic point of view. In recent years, we have been investigating such interaction using *in-situ* infrared spectroscopy to clarify the acid properties of the zeolite in atomic- and molecular-level. In the previous works, we have shown that N₂ adsorption on H-form zeolites gives two specific $\nu(\text{NN})$ bands at 2335 and 2352 cm⁻¹ that have been attributed to the N₂ species adsorbed on Brønsted acid sites and Lewis acid sites of the zeolites, respectively (WAKABAYASHI *et al.*, 1993a, b). The growth of the 2335-cm⁻¹ band is accompanied by the decrease of the $\nu(\text{OH})$ band at 3616 cm⁻¹ (the band due to the acidic OH groups) and the simultaneous growth of the $\nu(\text{OH})$ band at 3510 cm⁻¹ (due to the hydrogen-bonded OH-groups). That feature has been explained by the formation of hydrogen bonding between the adsorbed N₂ species that gives the 2335-cm⁻¹ band and the acidic OH groups that gives the 3616-cm⁻¹ band.

In one of the previous works (WAKABAYASHI *et al.*, 1993a), we conducted a band deconvolution of the observed $\nu(\text{OH})$ bands in order to see the behavior of the bands in detail. The band shape of each component band was assumed to be Gaussian type. Some discrepancy between the fitted curve and the observed spectrum was remained in the foot of the band although the well curve fitting was obtained in the main part of the band.

In the present work, we examine the effect of the band shape on the curve fitting of the $\nu(\text{OH})$ bands of the bare H-mordenite. Using the result, the $\nu(\text{OH})$ bands of N₂-adsorbed H-mordenite are deconvoluted.

2. Experimental

H-mordenite (Si/Al=10) was provided by the Catalysis Society of Japan. The zeolite powder was pressed into a self-supporting disk of 10 mg/cm². The disk was placed in a quartz-made IR cell that allows us *in-situ* sample treatment and IR measurement in the temperature range between 85 and 1000 K. The IR cell was attached to a conventional closed-circulation system. Its base pressure is less than 0.1 Pa, and is estimated to be less than 10⁻³ Pa. The sample disk was evacuated and treated with oxygen at 773 K for several hours. Finally, the sample disk was evacuated at 873 K and was used for the N₂ adsorption at 110 K.

N₂ (>99.9%) were purified by passing slowly through a cold trap at liquid-

nitrogen temperature to remove residual water and other impurities.

IR measurements were done with a Jasco FT/IR-7000 spectrometer using an MCT detector at a spectral resolution of 4 cm^{-1} and by averaging of 128 scans. FT-IR spectra of the clean disk were measured at low temperatures and were used as the background spectra. IR spectra of N_2 -adsorbed zeolite were measured after the adsorption equilibrium was achieved. IR spectra in the $\nu(\text{NN})$ are presented as difference spectra, and the $\nu(\text{OH})$ region in that of transmission mode. Other experimental conditions have been already described (WAKABAYASHI *et al.*, 1993a).

Band deconvolution was done using MacCurveFit 1.1. program written by Kevin Raner.

3. Results and Discussion

3.1 IR Spectra of Bare and N_2 -Adsorbed H-mordenite

IR spectra of the bare and N_2 -adsorbed H-mordenite at 110 K are shown in Fig. 1. As seen from Fig. 1b, two bands are observed at 2335 and 2352 cm^{-1} in the $\nu(\text{NN})$ region. This two bands showed different pressure- and temperature-dependence, indicating that their origin is different (WAKABAYASHI *et al.*, 1993a). As shown in Fig. 1a, the $\nu(\text{OH})$ band at 3616 cm^{-1} decreased with the increase of the N_2 pressure accompanied by the simultaneous growth of the band at 3510 cm^{-1} . Considering the

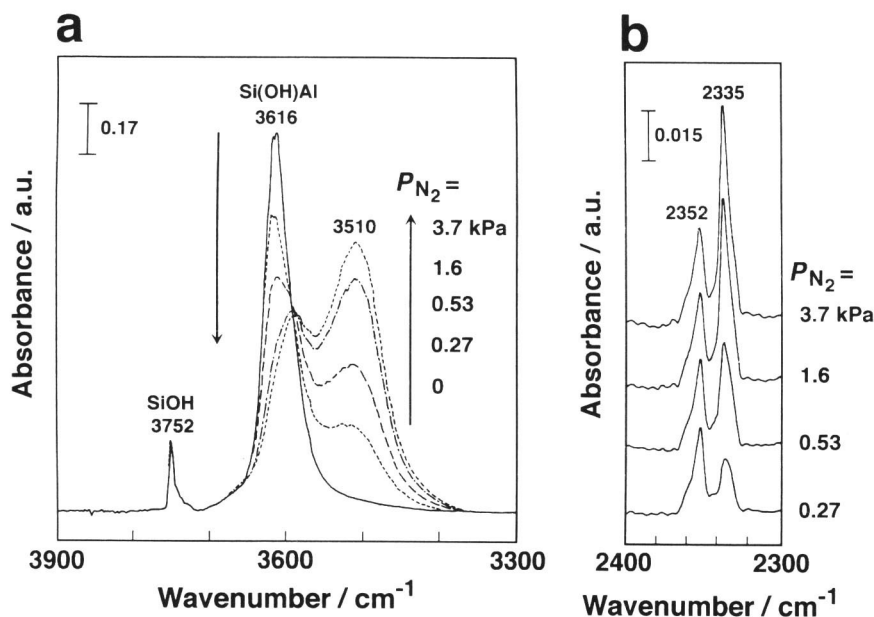
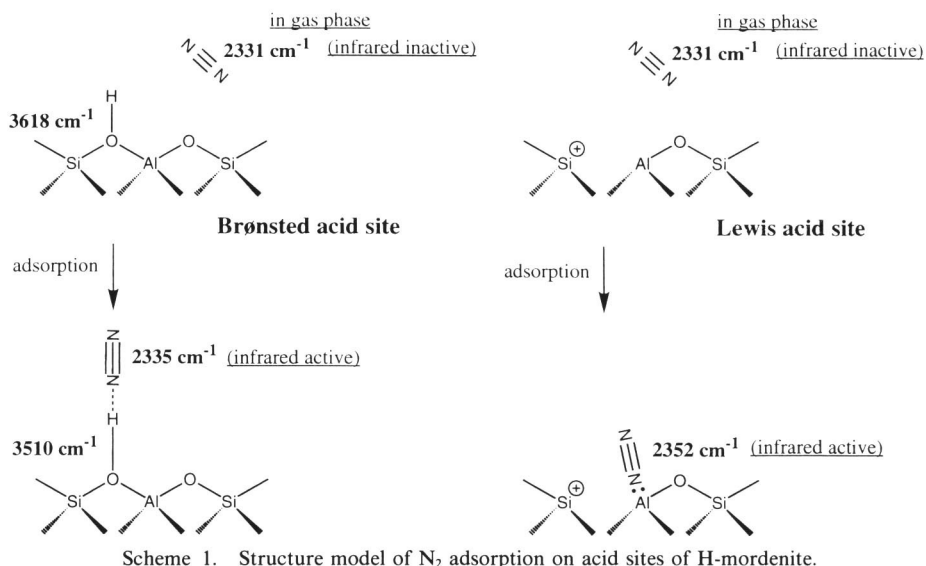


Figure 1. FT-IR spectra of N_2 -adsorbed H-mordenite at 110 K. (a) $\nu(\text{OH})$ bands, (b) difference spectra in the $\nu(\text{NN})$ region. The equilibrium pressures of N_2 are indicated in the Figure.



effect of water-vapor treatment and the correlation between the change of the band area of the $\nu(\text{NN})$ bands and those of the $\nu(\text{OH})$ bands, the 2335-cm^{-1} band has been assigned to the $\nu(\text{NN})$ band of the N₂ species adsorbed on Brønsted acid sites of the zeolite through hydrogen bonding, and the 2352-cm^{-1} band to that of the N₂ species adsorbed on Lewis acid sites (WAKABAYASHI *et al.*, 1993a). A structure model of the N₂ adsorption is shown in Scheme 1. In Scheme 1, the stretching frequency of the acidic OH groups is written as 3618 cm^{-1} reflecting the result of the band deconvolution as described in next sections.

3.2 Peak Deconvolution of the $\nu(\text{OH})$ Bands Observed for Bare H-mordenite

In this section, we describe the effect of the band shape on the curve fitting of the $\nu(\text{OH})$ band of the acidic OH groups at 3616 cm^{-1} observed for the bare H-mordenite.

Usually, IR bands are deconvoluted into either Gaussian shaped bands or Lorentzian bands (RYBERG, 1989). When the band width of single band is determined mainly by the lifetime broadening, its band shape is first approximated by a Lorentzian shape as expressed by the function as follows:

$$L(x) = \frac{k \cdot (\Delta/2)^2}{(x - x_0)^2 + (\Delta/2)^2} \quad (1)$$

where k , Δ , and x_0 are a constant, the full width at half maximum (FWHM), and the peak top frequency of the band, respectively. Δ has relation with lifetime, τ , as $\Delta = (2\pi c\tau)^{-1}$, where c is the speed of light. On the other hand, when the inhomogeneous broadening mainly determines the band width, its band shape is first approximated by a Gaussian shape as expressed as follows:

$$G(x) = k \cdot \exp\left(-\frac{\ln 2 \cdot (x - x_0)^2}{(\Delta/2)^2}\right) \quad (2)$$

where k , Δ , and x_0 have same meaning with Eq. 1.

In the case of the $\nu(\text{OH})$ bands of zeolites, their FWHM is usually in the range between 20 and 60 cm^{-1} . If the lifetime broadening is dominant, their lifetimes are, then, calculated to be between 265 and 88 fs. Such fast phenomena are incredible as usual vibrations. In fact, the vibrational lifetime of the $\nu(\text{OH})$ band of the acidic OH groups of H-mordenite has been measured to be 175 ± 7 ps at 145 K (FURUKI *et al.*, 1993). Therefore, it is natural to assume a Gaussian as band shape of component bands at first. In many cases, however, a Lorentzian shape or a mixture of Gaussian and Lorentzian are considered in practice to obtain better curve fitting (LAMBERTI *et al.*, 1993).

At first, the $\nu(\text{OH})$ band of the acidic OH groups is deconvoluted into two Gaussian component bands following the previous work (WAKABAYASHI *et al.*, 1993a). As shown in Fig. 2a, some discrepancy is remained in the foot of the 3616- cm^{-1} band although well curve fitting is achieved in the central part of the band. In order to gain a better fitting in the foot, the 3616- cm^{-1} band is deconvoluted into two Lorentzian bands. As seen in Fig. 2b, a better fitting is achieved although some discrepancy is remained in the higher frequency part. The best curve fitting is achieved when the higher frequency component is deconvoluted to a Gaussian and the lower frequency component is to a Lorentzian, as shown in Fig. 2c. The higher frequency component band at 3618 cm^{-1} has been assigned to the $\nu(\text{OH})$ band of the bridging OH groups in the main channel of mordenite and the lower frequency one at 3600 cm^{-1} has been to that of the bridging OH groups in the small channel (WAKABAYASHI *et al.*, 1993a;

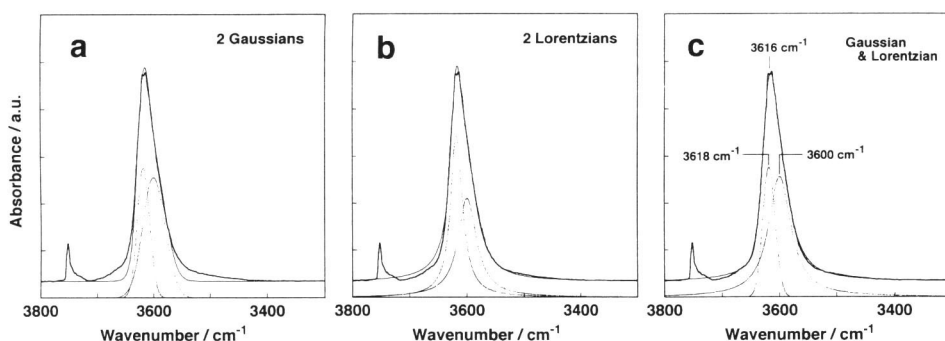


Figure 2. Effect of the band shape on the band deconvolution of the $\nu(\text{OH})$ band of the acidic OH groups at 3616 cm^{-1} observed for the bare H-mordenite at 110 K. The $\nu(\text{OH})$ band is deconvoluted to (a) two Gaussians, (b) two Lorentzians, and (c) a Gaussian for higher frequency component band and a Lorentzian for lower frequency component band. Deconvoluted bands and their sum are drawn by broken lines and thin solid lines, respectively. The original spectra are drawn by thick solid lines.

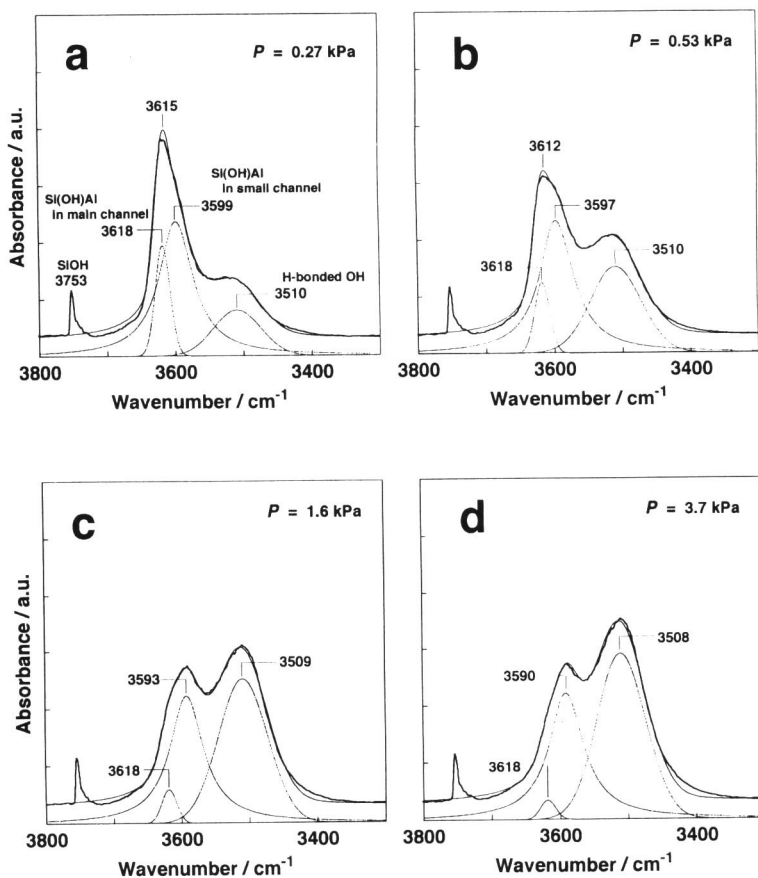


Figure 3. A result of band deconvolution of the $\nu(\text{OH})$ bands observed for the N_2 -adsorbed H-mordenite at 110 K. The equilibrium pressure of N_2 is (a) 0.27 kPa, (b) 0.53 kPa, (c) 1.6 kPa, and (d) 3.7 kPa. The meaning of the lines is the same as those of Fig. 2.

Table 1. Deconvoluted $\nu(\text{OH})$ bands obtained for the bare and N_2 -adsorbed H-mordenite at 110 K.

$P(\text{N}_2)$ (kPa)	OH in main channel			OH in small channel			H-bonded OH		
	$\nu(\text{OH})$	FWHM	Band area	$\nu(\text{OH})$	FWHM	Band area	$\nu(\text{OH})$	FWHM	Band area
0	3618	25.5	14.1	3600	46.4	23.8	—	—	—
0.27	3618	25.5	9.93	3599	60.2	28.5	3510	81.0	13.1
0.53	3618	25.5	6.30	3597	60.3	28.1	3510	88.0	26.7
1.6	3618	25.5	2.92	3593	59.2	26.4	3509	84.5	42.6
3.7	3618	25.5	1.66	3590	61.0	27.0	3508	83.1	48.3

$\nu(\text{OH})$ and FWHM are presented in cm^{-1} , and band area is in arbitrary unit.

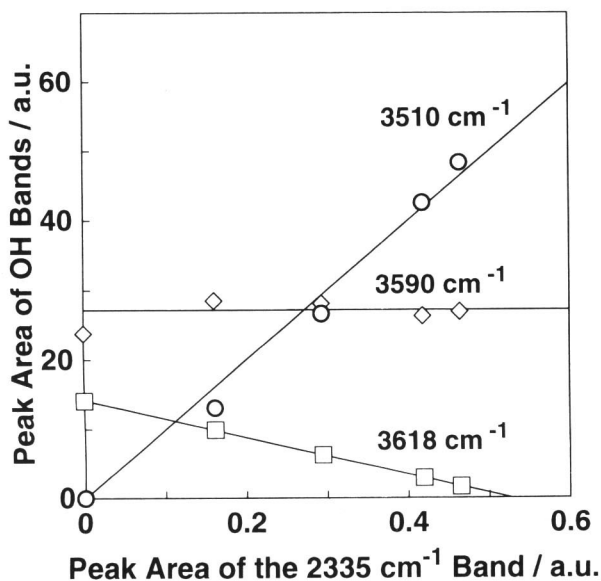


Figure 4. Correlation between the integrated absorbance of the $\nu(\text{NN})$ band at 2335 cm^{-1} and those of the $\nu(\text{OH})$ bands at 3618 , 3590 , and 3510 cm^{-1} .

ZHOLOBENKO *et al.*, 1993).

3.2 Peak Deconvolution of the $\nu(\text{OH})$ Bands Observed for N_2 -adsorbed H-mordenite

We here adopt Gaussian shape as the higher frequency component band and Lorentzian shape as the lower frequency component band of the 3616 cm^{-1} band following the result described above. The best fitting is achieved when the band shape of hydrogen-bonded OH groups is assumed to be Gaussian as shown in Fig. 3. In the curve fitting, it is assumed that the peak-top frequency and FWHM of the 3618 cm^{-1} band do not change with the increase of the N_2 pressure. As seen from Fig. 3, well curve-fittings are achieved, indicating the validity of our assumption. The result of the curve fitting is tabulated in Table 1 as well as that for bare H-mordenite.

Thus obtained integrated absorbances of the component $\nu(\text{OH})$ bands are plotted against that of the $\nu(\text{NN})$ band at 2335 cm^{-1} , as shown in Fig. 4. This figure clearly shows the linear correlation between the decrease of the peak area of the 3618 cm^{-1} band and the increase of that of the 2335 cm^{-1} band as well as between the increase of that of the 3508 cm^{-1} band and the increase of that of the 2335 cm^{-1} band. This result shows apparently the formation of 1:1 hydrogen-bonded complex between the N_2 species that gives the 2335 cm^{-1} band and the acidic OH groups in the main channel of H-mordenite (WAKABAYASHI *et al.*, 1993a). On the other hand, the $\nu(\text{OH})$ band at 3590 cm^{-1} is almost constant for the increase of N_2 pressure, suggesting the weak interaction between the bridging OH groups in small channel of H-mordenite and the adsorbed N_2 species (WAKABAYASHI *et al.*, 1993a).

4. Summary

Band deconvolution of the $\nu(\text{OH})$ bands observed for the bare and N_2 -adsorbed H-mordenite at 110 K is re-examined. Considering the effect of the band shape on the deconvolution, the best curve fitting of the acidic OH band at 3616 cm^{-1} is obtained when the band is deconvoluted to a Gaussian shaped band at 3618 cm^{-1} and a Lorentzian shaped band at 3600 cm^{-1} . Using this result, the $\nu(\text{OH})$ bands observed for the N_2 -adsorbed H-mordenite at 110 K are deconvoluted. The decrease of the $\nu(\text{OH})$ band at 3618 cm^{-1} and the increase of the $\nu(\text{OH})$ band at 3510 cm^{-1} are linearly correlated with the increase of the $\nu(\text{NN})$ band at 2335 cm^{-1} , which clearly shows the formation of 1 : 1 hydrogen-bonded complex between acidic OH groups of H-mordenite and the N_2 species that gives the $\nu(\text{NN})$ band at 2335 cm^{-1} .

Acknowledgement

This work was partly supported by the Grant-in-Aid for Scientific Research (No. 06640760) from the Ministry of Education, Science and Culture, Japan. The authors would like to express their grateful acknowledgement to the Catalysis Society of Japan for providing H-Mordenite sample. The authors also express their thankfulness to Dr. Akihide Wada of Tokyo Institute of Technology for providing a personal-computer program for digitizing IR-spectrum charts.

References

- FURUKI, M., J. KUBOTA, Y. GOTO, F. WAKABAYASHI, J. KONDO, A. WADA, K. DOMEN and C. HIROSE, 1993. Vibrational lifetime of surface species of zeolites by picosecond IR pulses. *J. Electronspectrosc. Relat. Phenom.*, **64/65**: 259–267.
- LAMBERTI, C., C. MORTERRA, S. BORDIGA, G. CERRATO and D. SCARANO, 1993. Band resolution techniques and Fourier transform infrared spectra of adsorbed species. *Vib. Spectrosc.*, **4**: 273–284.
- RYBERG, R., 1989. Infrared study of molecules adsorbed on metal surfaces. In *Advance in Chemical Physics*, K. P. Lawley Ed., John Wiley & Sons, New York, pp. 1–44.
- WAKABAYASHI, F., J. KONDO, A. WADA, K. DOMEN and C. HIROSE, 1993a. FT-IR studies of the interaction between zeolitic hydroxyl groups and small molecules. 1. Adsorption of nitrogen on H-mordenite at low temperatures. *J. Phys. Chem.*, **97**: 10761–10768.
- WAKABAYASHI, F., J. KONDO, K. DOMEN and C. HIROSE, 1993b. Dinitrogen as a probe of acid sites of zeolites. *Catal. Lett.*, **21**: 257–264.
- ZHOLOBENKO, V. L., M. A. MAKAROVA and J. DWYER, 1993. Inhomogeneity of Brönsted acid sites in H-mordenite. *J. Phys. Chem.*, **97**: 5962–5964.