

SER Spectrum: A Novel Information Imaging to Characterize Molecular Dynamics of NO₂ on Na–Mordenite

Haitao Li,^{*,†} Hidenori Yahiro,[‡] Masaru Shiotani,[‡] and Anders Lund[†]

Chemical Physics Laboratory, Department of Physics and Measurement Technology, Linköping University, S-581 83, Sweden, and Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi Hiroshima 739-8527, Japan

Received: January 5, 1998; In Final Form: March 25, 1998

A novel three-dimensional information imaging, spin exchange rate (SER) spectra, was proposed to use for the analysis of complicated molecular motions of gaseous molecules in powder solids. It has successfully been applied to characterize molecular dynamics of NO₂ on Na–mordenite. This spectrum directly illustrates the detailed dynamic information of motion of NO₂ versus temperature, which showed that (1) the molecular motion of NO₂ is a superposition of individual motions, corresponding to different spin exchange rates; (2) for a given temperature, there is a dominant spin exchange rate and the rate increases with increasing temperature; (3) the distribution of active spin exchange rates is broadened with increasing temperature and then decreases again at higher temperature; and (4) there are two different dynamical processes in the temperature range 110–260 K: one with an activation energy of 486 J/mol is attributed to adsorption; the other with 4390 J/mol is a desorption process, and they reach adsorption–desorption equilibrium. Theoretical interpretations of these observations are also given in this paper.

Introduction

The understanding of the molecular dynamics of gaseous molecules on a catalyst surface is very important to characterize the performance of the catalyst.¹ However, in zeolitic catalysts, which have the most potential for removal of NO_x from the exhaust of automobiles,^{2–11} the molecular motion in the pores is poorly understood.¹ The sizes of the pores are so small that no relevant method can directly measure molecular motion inside the zeolite. Recently, NO₂ was selected as a paramagnetic probe to investigate the dynamics of gaseous molecules on the zeolite surface by ESR (electron spin resonance). The early studies^{12–17} of NO₂ in the adsorbed states and in solid media were limited to qualitative analysis of ESR spectra. The first attempt with a quantitative analysis was made by Pietrzak and Wood,¹⁸ although without modern motional calculation models. The motional dynamics of NO₂ on Vycor glass were successfully measured and quantitatively analyzed by Shiotani and Freed based on slow-motion ESR theory.¹⁹ Since then, the slow-motional theory has become a standard method to analyze the motional dynamics of NO₂ in the gas–solid interfaces.^{19–27} This theory characterizes several different dynamic models such as Brownian rotational diffusion, non-Brownian rotational diffusion, and Heisenberg spin exchange.^{20,21} The computer simulation with slow-motion theory is used to extract the magnetic and dynamic information by fitting the models to the experimental spectra. The magnetic information is mainly described by hyperfine (**A**) and **g** tensors. The dynamic information obtained is diffusion rates of rotation about NO₂ molecular axes or Heisenberg spin exchange rates between NO₂ molecules. The molecular motion of NO₂ on the surface is mainly concluded to be due to rotational diffusion and/or

translational diffusion. Shiotani and co-workers reported that the dynamics of NO₂ show mainly rotational motion in the large pore and cage structure of solids.^{19,25,26} Kevan et al.²² also reported a similar rotational motion of NO₂ as an impurity in SiO₂ thin films. Our current results^{23,24,26,27} indicate that the Heisenberg spin exchange between molecules due to translational diffusion of NO₂ makes a predominant contribution to the motional dynamics in the zeolites with channel structure, e.g., mordenite, ZSM-5, and L-type. The Heisenberg spin exchange rate is proportional to the diffusion rate of NO₂ in the channels. However, due to the complex dynamics of NO₂ on the gas–solid interface,^{19,22} there is usually a mismatch between the experimental data and simulations. One of the main goals of this paper is to reveal this complex dynamics.

The normal procedure to study the motional dynamics of NO₂ adsorbed on Na–mordenite (denoted as Na–Mor in the following sections) is to record a series of ESR experimental spectra at different temperatures and then to get the Heisenberg spin exchange rate(s) by comparison with the experimental spectrum. The spin exchange rate(s) representing the diffusion rate of NO₂ in this paper is a hidden quantity, which is not directly measurable. A conventional way to handle this is to utilize the computer simulation method to indirectly estimate the spin exchange rate(s). More specifically, for each experimental ESR spectrum, a simulated ESR spectrum based on the slow-motion theory is obtained by using an assumed spin exchange rate(s). If the assumed spin exchange rate is correct, then the simulated spectrum should match the experimental one very well. If mismatch occurs, the assumed spin exchange rate has to be adjusted until the simulated spectrum matches the experimental one. This method has been used to estimate spin exchange rate(s) in different zeolites.^{23–27} However, some problems are observed when employing this method. Typically, the choice of the best spin exchange rate is not done in a systematic way and is visually chosen. We have to manually

* Corresponding author: haitao@ifm.liu.se.

[†] Linköping University.

[‡] Hiroshima University.

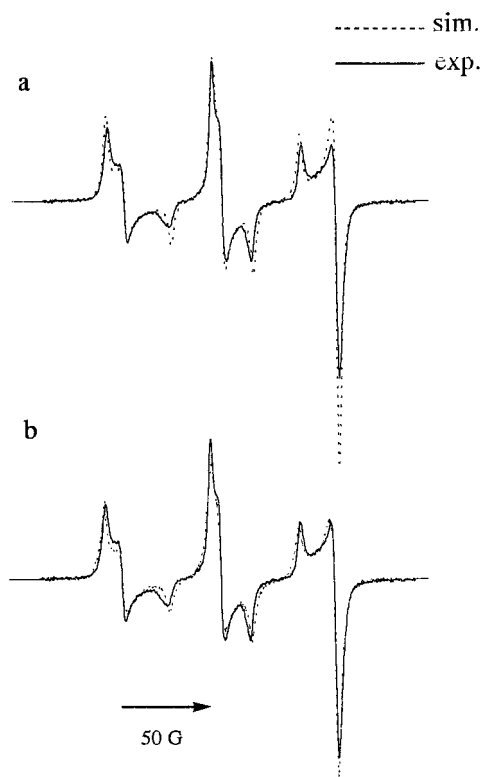


Figure 1. Simulated spectra compared with the experimental one measured at 116 K. (a) Simulation with single spin exchange rate, $26 \times 10^6 \text{ s}^{-1}$. (b) Simulated spectrum obtained by the eigenspectra method.

and randomly search a suitable spin exchange rate; the simulated spectrum with a single spin exchange rate is sometimes not in very good agreement with the experimental one, as shown in Figure 1a. In addition, more than one rate often exists which gives simulated spectra showing similar agreement with the experimental one, as shown in Figure 2a,b. Therefore, there is an ambiguity in specifying a single spin exchange rate for given experimental spectra in a certain temperature range. These problems reveal that the implicit assumption that only a single spin exchange rate for a given temperature exists is questionable. In this paper, a novel information imaging spin exchange rate (SER) spectrum, which is based on the assumption that an experimental spectrum is specified by a superposition of individual spin exchange rate(s), is proposed to characterize the detailed motional dynamics of NO_2 on Na-Mor. To our best knowledge, no relevant research to obtain detailed motional information of NO_2 on Na-Mor has been reported yet.

The SER spectrum based on eigenspectra is actually a statistical method to determine the individual rate components from the powder NO_2 ESR spectrum. It is normally difficult with spectroscopic methods to study the individual components and/or the correct number of constituents from the powder spectrum.^{28,33,34} In the chemical and physical applications of ESR spectroscopy, the use of least-squares analysis (LS),³⁰ principal component analysis (PCA),^{31–34} and maximum-likelihood common-factor analysis (MLCFA)^{28,29} has provided rather good results. Lindgren et al.³⁰ applied a LS method to study the abundance of folded, folding intermediate, and unfolded structures of human carbonic anhydrase (HCA 11) depending on the degree of denaturation of Gu-HCL in the region 0–4 M. MLCFA was used to characterize the multiple components (up to 7) of the powder ESR spectra.²⁸ An advantage of the latter method is that the different components could be characterized by their hyperfine and *g* tensors (totally

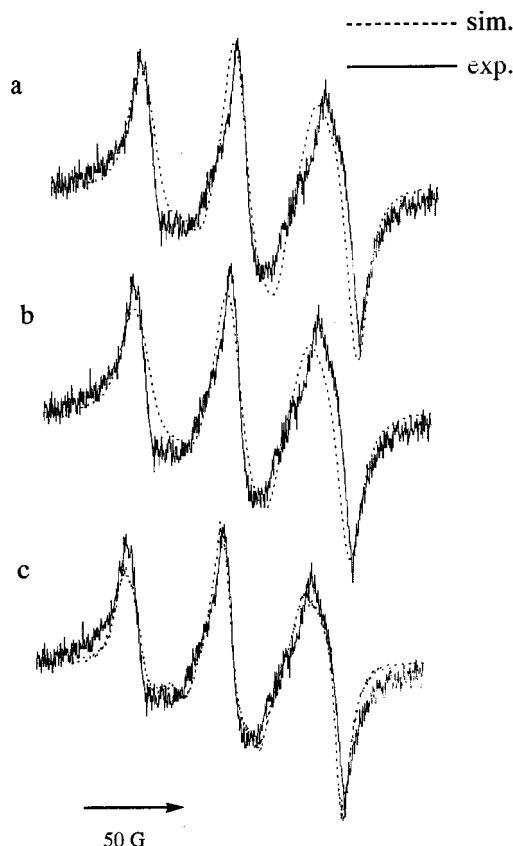


Figure 2. Simulated spectra with the single spin exchange rates and SER method compared with the experimental one measured at 209 K. Simulations with single spin exchange rate, $243 \times 10^6 \text{ s}^{-1}$ (a) and with $278 \times 10^6 \text{ s}^{-1}$ (b) were performed. The simulated spectrum (c) was obtained by the eigenspectra method.

four radicals were identified in ^{13}C -enriched apatite powder). The SER method presented in this work is closely related to the PCA method and is simpler to implement than the MLCFA. It is also adequate for the purpose of obtaining the rate distribution of NO_2 undergoing Heisenberg exchange from the ESR spectra.

In the following sections, we first give a theoretical basis of SER spectrum and then describe how to obtain and interpret SER spectra.

SER Spectrum. A reasonable assumption is that multiple spin exchange rates coexist for a given temperature. If we take the single spin exchange rate as a SER spectrum component, then the experimental ESR signal should have a distribution of spin exchange rates according to this assumption.

The spin exchange rate spectra $\{a_r\}$ are defined as

$$a_r = \sum_{k=1}^M \alpha_k \beta_{kr} \quad (1)$$

Here a_r is a single SER spectrum corresponding to the spin exchange rate "*r*"; *M* is the number of eigenspectra to be described; α_k and β_{kr} are two kinds of weights. The value of α_k is calculated as follows:

$$\alpha_k = \sum_{m=1}^N y(m) \phi_k(m) \quad (2)$$

Here $\{y(m)\}$ is the experimental ESR spectrum containing *N* points obtained at a certain temperature. $\{\phi_k(m)\}$ are the eigenspectra and ϕ_k is the *k*th eigenspectrum. Obviously, α_k is

the projection of $\{y(m)\}$ on the eigenspectrum ϕ_k . The eigenspectra $\{\phi_k(m)\}$ can be extracted from the simulated spectra $\{x_r(m)\}$ by well-known linear algebra methods.^{33,34,36} The treatment gives the eigenspectra as in eq 3.

$$\phi_k(m) = \sum_{r=1}^P \beta_{kr} x_r(m) \quad (3)$$

P is the number of spin exchange rates; x_r is the simulated spectrum corresponding to the spin exchange rate r ; and β_{kr} specifies the contribution of the simulated ESR spectrum x_r to the k th eigenspectrum ϕ_k . The number P of chosen $x_r(m)$ determines the resolution of the SER spectrum. If we take a simulated spectrum as a vector, then all simulated spectra will be within a subspace, the SER spectrum space. Since there is a rich redundancy among the waveforms of the spectra, the SER spectrum space can be low-dimensionally represented in the eigenspectra basis. Only the eigenspectra corresponding to the five largest eigenvalues (denoted as top five in the following sections) were found necessary to include in the present case, one-tenth of the number of simulated spectra. This is the reason the eigenspectra are introduced in this paper.

Experimental Section

Sample Preparation. Na–Mor zeolite with SiO₂/Al₂O₃ ratio = 10 was obtained from Tosoh Co. in Japan. NO₂ was obtained commercially and used without further purification. Na–Mor (0.05 g) was activated in an ESR sample tube of diameter 4 mm at 200 °C for 1 h in air and at 500 °C for 3 h under vacuum. The sample was then cooled to 0 °C and exposed to 40 Torr of NO₂ until equilibrium was established. Then the sample tube was sealed.

ESR Measurement. ESR measurements at 77–260 K were performed on a Bruker ER-200D ESR spectrometer operating at the X-band with 100 kHz field modulation and with the 90 dB attenuation low-power option. The microwave power was adjusted to obtain spectra that were not saturated. The magnetic field was calibrated with a Bruker ER 035 NMR gaussmeter. The Bruker VT 4111 liquid nitrogen control system allowed the temperature to be reduced to 110 K.

Results and Discussion

Spectra Preparation. Fifty-one experimental ESR spectra of NO₂ on Na–Mor were recorded from 110 to 260 K with a step of 3 K. Fifty simulated ESR spectra were calculated by employing the Heisenberg spin exchange model with spin exchange rates from 5×10^6 to 348×10^6 s⁻¹, a step of 7×10^6 s⁻¹ and a line width of $1/T_2^0 = 0.1$ mT.

Eigenspectra. The waveform of a simulated ESR spectrum is governed by the inherent properties of the paramagnetic NO₂ molecules and their surrounding environments. It contains the magnetic and dynamic information of NO₂ on zeolites.^{21,22,35} To represent experimental spectra with associated simulated spectra, we have to extract the intrinsic properties from the ensemble of the simulated spectra because the number of simulated spectra generated is too large to be handled reasonably. The eigenspectra capture the intrinsic properties from simulated spectra in a statistically optimal sense.

Eigenspectra of the simulated NO₂ spectra were calculated according to eq 3. The top five principal ones as shown in Figure 3 are used to synthesize the experimental spectrum. The simulation results are in good agreement with experimental spectra as shown in Figures 1b and 2c. The simulation with

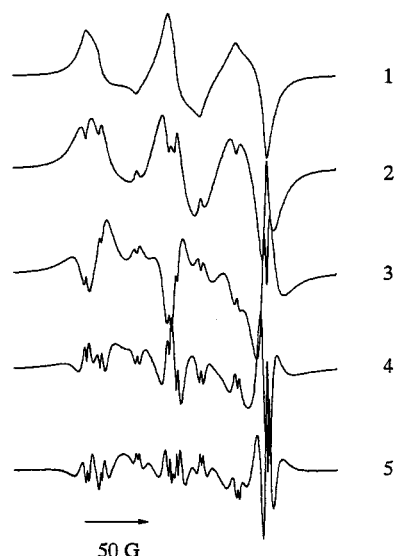


Figure 3. Top five eigenspectra extracted from 50 simulated ESR spectra with single spin exchange rates in the range 5×10^6 to 348×10^6 s⁻¹.

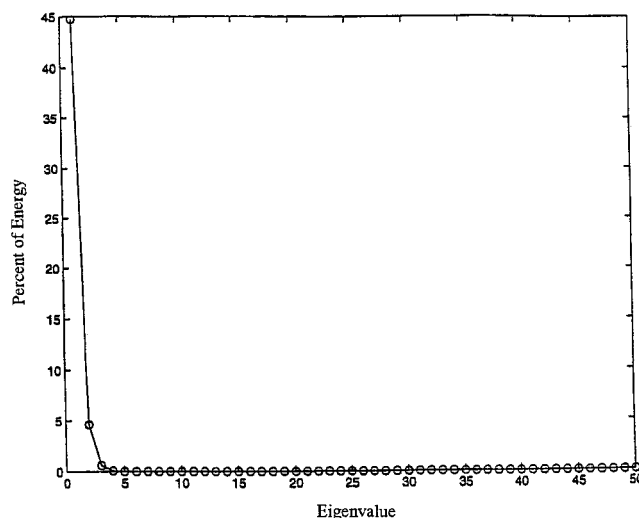


Figure 4. Signal energy distribution of the eigenspectra. The signal energy of eigenspectra decreases quickly and then stays very small and constant.

only the top three or four eigenspectra gives worse agreement. Simulations with more eigenspectra (e.g., top seven or 10) did not provide better simulation results than that with the top five. The signal energy distribution is shown in Figure 4, from which it can be seen that the top five ones contain almost 95% of the signal energy. This means that five eigenspectra can sufficiently represent the simulated spectra and that a further improvement in synthesis performance by using more eigenspectra cannot be expected. Although the effective number of eigenspectra is small, only five here, they contain the information associated with the whole range of spin rates. This is reflected in eq 3, which tells that an eigenspectrum is a superposition of simulated spectra covering the whole range of spin exchange rates. The superposition information (SI) is described by the weight β_{kr} and that of the top five eigenspectra is shown in Figure 5. SI 1 displays that eigenspectrum 1 has major contributions from the whole range of spin exchange rates. SI 2 has its main contribution from those spin exchange rates between 2×10^8 and 3.48×10^8 s⁻¹. The SI for the other eigenspectra can be characterized in a similar way.

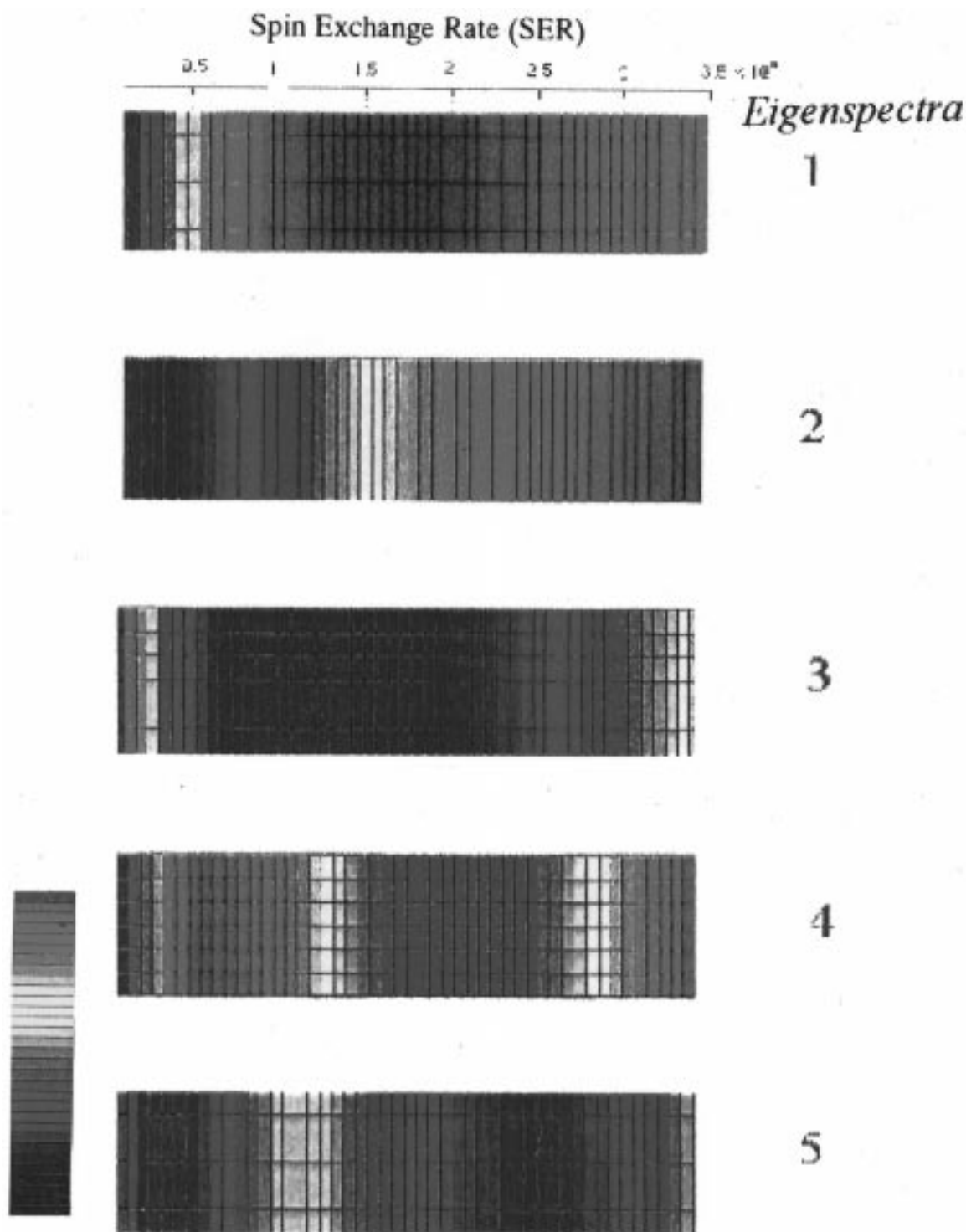


Figure 5. Color map of the top five eigenspectra described by the contribution of the whole range of single spin exchange rates. The different colors represent various contributions of the single spin exchange rate: blue = low, red = high contributions.

In summary, the eigenspectra have different contributions to spin exchange rates. The top five eigenspectra take care of the whole range of spin exchange rates in an optimal way. Eigenspectra used here act as an intermediate to aid the search of active spin exchange rates for a given experimental spectrum. The topics such as what is the physical meaning of the eigenspectra themselves and how to use eigenspectra to characterize the inherent properties of paramagnetic molecules and surfaces of zeolites are under investigation and beyond the theme of this paper.

Interpretation of the SER Spectrum. For a given experimental spectrum, a simulated spectrum can be synthesized by using eigenspectra.

$$\hat{y}(m) = \sum_{k=1}^M \alpha_k \phi_k(m) \quad (4)$$

Here $\hat{y}(m)$ is the simulated spectrum synthesized from the eigenspectra and α_k is computed by using eq 2. Two examples are shown in Figure 1b and Figure 2c. In comparison with the

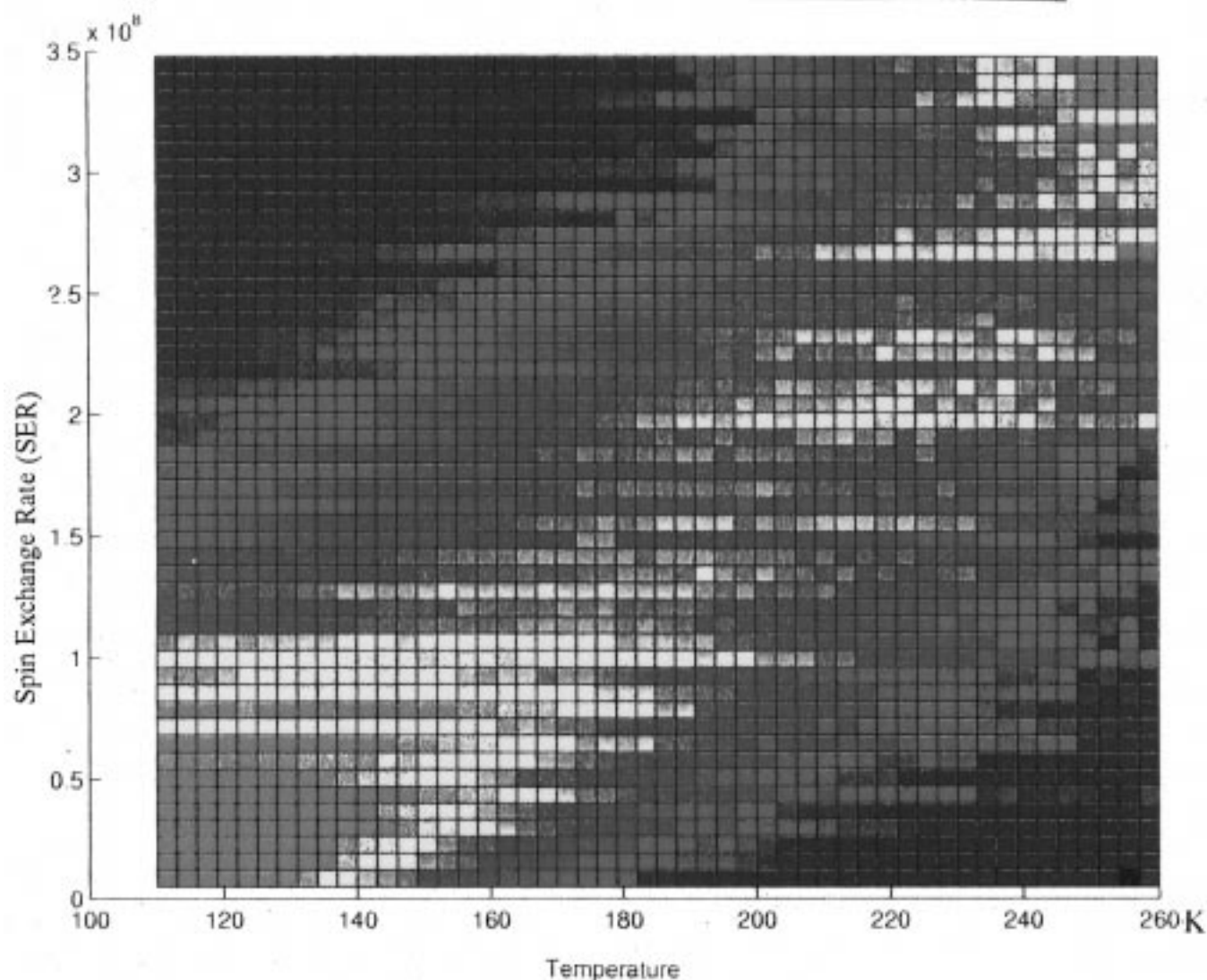


Figure 6. SER-T spectrum describing the spin exchange rates depending on the temperature between 110 and 260 K in NO₂/mordenite. Two red regions indicate the two independent kinetic processes described in the text.

simulated spectrum generated from the traditional simulation method, the spectrum is much closer to the experimental spectrum. This verifies the assumption that the molecular motion of NO₂ is a superposition of individual motional components, corresponding to different spin exchange rates.

This clearly extends the assumption that the molecular motion of NO₂ is governed by a single motional component. High-resolution dynamic information about molecular motion is provided by the eigenspectra. Since the weights α_k and $\beta_{k,r}$ are both available, the SER spectrum can be built according to the definition of eq 1. The SER spectrum automatically displays the active spin exchange rates and their strengths. To have a good visualization, the strengths are coded with colors, in which the red means high weight value and the blue is low weight value. To obtain the relation between the spin exchange rates and temperature (T), a SER-T spectrum is obtained by displaying the SER spectra generated at different temperatures. A SER-T spectrum is shown in Figure 6, which provides the detailed dynamic information about the molecular dynamics of NO₂ on Na-Mor between 110 and 260 K. From this spectrum the following observations can be obtained:

(i) The active spin exchange rates increase with increasing in the temperature.

(ii) Two significant red regions illustrate that the active spin exchange rates are dominant at low and high temperatures. A quantitative measure of the dominance will be given in the following section.

(iii) At the temperature range from 162 to 238 K, the active spin exchange rates are widely distributed. There are no dominant active rates.

These observations give a clear picture of the molecular motion at different temperatures. Further physical interpretation of these observations will be given later.

Dominant Heisenberg Spin Exchange Rate (DSER). For a given experimental spectrum, more than one spin exchange rate can be estimated. More importantly, not only the rates but also their strengths are identified. The strength reflects the contribution of each spin exchange rate to the experimental spectrum. To characterize the spin exchange distribution of an ESR spectrum at a given temperature, the dominant Heisenberg spin exchange rate (DSER) is employed. The DSER is an average quantity of the top n spin exchange rates, which have

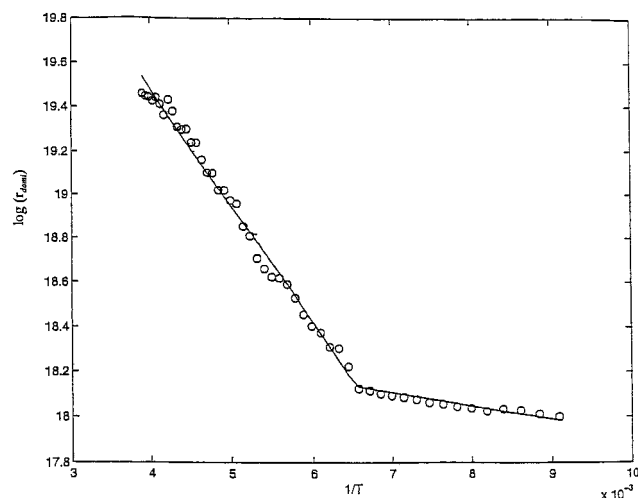


Figure 7. Arrhenius plot of $\log(r_{\text{domi}})$ against $1/T$ for the NO_2/Mor system.

the largest contributions at a given temperature. The number n depends on the width of the distribution; in the present investigation n was chosen empirically. If the assumption is made that a given experimental spectrum contains a single spin exchange rate(s), then the dominant rate in the SER spectrum should correspond to the rate obtained by the conventional approach. This illustrates that the result obtained by the conventional approach based on computer simulation is compatible with the SER spectrum. The dominant rate is obtained by the average of the top n spin exchange rates r_i after normalization of the SER spectra a_r . The normalization is done as

$$a'_r = \frac{a_r}{\sum_{r=1}^P a_r} \quad r = 1, \dots, P \quad (5)$$

The dominant rate r_{domi} was calculated as

$$r_{\text{domi}} = \frac{\sum_{r=1}^n r_i a'_r}{\sum_{r=1}^n a_r} \quad (6)$$

r_1, \dots, r_n are the top n spin exchange rates.

The dominant rate can be applied to describe dynamic processes, which have a wide rate distribution similar to the present case. To estimate the activation energy in NO_2/MOR , the dominant r_{domi} was used in the Arrhenius equation. The Arrhenius plot of $\log(r_{\text{domi}})$ against $1/T$ is shown in Figure 7. It is obvious that two kinetic processes are involved in the NO_2/Mor system between 110 and 260 K. To evaluate the activation energy, a least-squares (LS) fitting was used. Since the dominant rates have different strengths, as shown in Figure 8, good fitting methods should prefer the rates with high strengths. Thus a weighted LS fitting technique is used to evaluate the activation energy in this paper. The estimated activation energies are 4390 and 486 J for the higher and lower temperature ranges, respectively. An explanation about this is described below.

Adsorption–Desorption of NO_2 on the Surface. Based on the above SER spectra, the following conclusions for the molecular dynamics of NO_2 on Na–Mor were made.

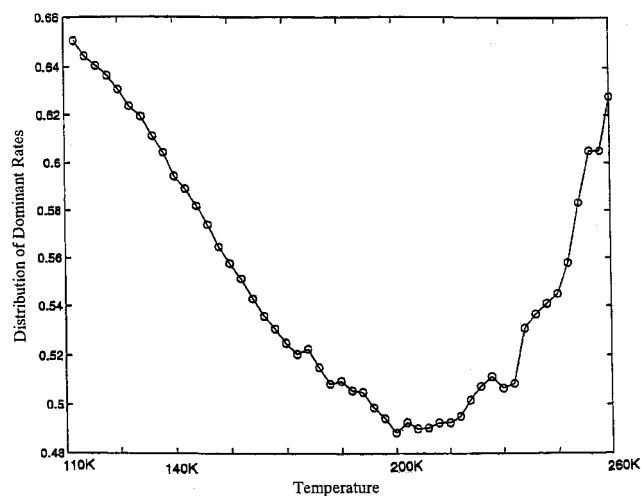


Figure 8. Distribution of the dominant spin exchange rate in the temperature range 110–260 K.

- (i) Molecular motion is a superposition of individual motional components.
- (ii) The active spin rates depend on temperature.
- (iii) The active dominant rate also shows temperature dependence.
- (iv) Two different kinetic processes exist.

As mentioned above, it is reasonable to assume that not all molecules have the same motional rate; there is a distribution of motional rates, and the particular distribution depends on the conditions of the system.⁴⁰ The molecular dynamic processes of NO_2 occurring on the surface of Na–Mor consist of four stages: diffusion of NO_2 to the surface, adsorption on the surface, desorption from the surface, and diffusion of NO_2 away from the surface. At a given temperature all four stages coexist at the same time. The adsorption and desorption are two different types of dynamic processes. This may result in the diversity in the motion rate. Furthermore there are different adsorption sites^{37–39} for NO_2 on the surface of Na–Mor, which lead to different motional rates. When molecules with different motional rates collide to exchange their spin states,^{23,27} different spin exchange rates occur. Therefore, it is reasonable to assume that the molecular motion shown in the ESR spectrum is a superposition of individual motion components.

There are two red regions appearing in Figure 6. This can be explained by assuming that they correspond to two independent dynamic processes shown in the Arrhenius plot of Figure 7. The first one occurs below 162 K. This is attributed to an adsorption process with Heisenberg spin exchange occurring between NO_2 molecules adsorbed on the surface. The different spin exchange rate(s) may be attributed to the different adsorption strengths. The adsorption strength may not have a wide distribution since NO_2 is physically adsorbed on the surface of the zeolite.¹⁹ The effect of adsorption strengths on the exchange rates will therefore be concentrated in a narrow range.

The second red region in Figure 6 above 248 K may be explained by assuming an adsorption–desorption equilibrium process. Due to thermal motion of NO_2 molecules, almost all NO_2 molecules are in a motional state with similar rates. The adsorption–desorption process can be controlled by only a few NO_2 molecules with relatively low rates. In both above cases, there is a dominant spin exchange rate because there is a dominant motional process affecting the motional rates of NO_2 . An important conclusion here is that in these two temperature ranges the simulated spectrum generated with a single spin

exchange rate should be close to the experimental one, as has in fact been found in Figure 1a.

In the temperature range 162–248 K there is no obvious spin exchange rate dominant region as shown in Figure 8. The motional rate of NO₂ has a wide distribution. There are several factors that affect the motional rates of NO₂ in this range. Typically, they are adsorption, desorption, various adsorption sites, and the hindrance from cations. Such factors give rise to many more individual motional components than those in the two red regions as shown in Figure 6. The motional dynamic process in this range is attributed to a desorption process of NO₂. The desorption rate of NO₂ on Na–Mor is roughly estimated to be $(1-3) \times 10^8 \text{ s}^{-1}$.

We have assumed that in the adsorption process the rate of NO₂ motion on the surface of Na–Mor is slow. The major kinetic process should be spin state exchange occurring between neighbor NO₂ molecules. This can be a reason its activation energy is as low as 486 J/mol in the present system. In the desorption process the NO₂ molecules need more energy to be desorbed from the surface. This corresponds to the evaluated activation energy, 4390 J/mol, almost 10 times higher than that in the adsorption state. These arguments are supported by the previous experimental result.²³

Concluding Remarks

The spin exchange rate (SER) spectrum provides detailed information on the translational diffusion of NO₂ adsorbed on Na–Mor. The obtained motional dynamics can be well explained from the adsorption and desorption processes point of view. The information spectrum is very valuable for practical applications in the study of the dynamical processes in porous materials depending on chemical modifications as, for example, the SiO₂/Al₂O₃ ratio, the different pore structures of zeolites, and so on. The SER technique based on the eigenspectrum method therefore has a potential for the more general understanding of the behavior of small gaseous molecules on a catalyst. Further dynamic investigation of gas molecules on catalyst surfaces by means of this new method is ongoing by the present authors.

Acknowledgment. The work was supported by grants from the Swedish National Technical Research Board (TFR) and The Swedish Foundation for International Cooperation in Research and Higher Education (STINT).

References and Notes

- (1) Gates, B. *Catalytic Chemistry*; John Wiley & Sons: New York, 1992.
- (2) Shelef, M. *Chem. Rev.* **1995**, *95*, 209.
- (3) Iwamoto, M.; Hamada, H. *Catal. Today* **1991**, *10*, 57.
- (4) Iwamoto, M.; Yahiro, H. *Catal. Today* **1994**, *22*, 5.
- (5) Li, H.; Lund, A. *Technical Report*, LiTH–IFM-R215; Linköping University, 1996.
- (6) Iwamoto, M.; Yahiro, H.; Yu-u, Y.; Shundo, S.; Mizuno, N. *Shokubai (Catalyst)* **1990**, *32*, 430.
- (7) Li, H.; Biglino, D.; Erickson, R.; Lund, A. *Chem. Phys. Lett.* **1997**, *266*, 417.
- (8) Li, Y.; Armor, J. U.S. Patent 5149512, 1992.
- (9) Li, Y.; Armor, J. *Appl. Catal. B, Environ.* **1992**, *1*, L31.
- (10) Tabata, T.; Kokitsu, M.; Ohtsuka, H.; Okada, O.; Sabatina, L.; Bellussi, G. *Catal. Today* **1996**, *27*, 91.
- (11) Amiridis, M.; Zhang, T.; Farrauto, T. *Appl. Catal. B, Environ.* **1996**, *10*, 203.
- (12) Zeldes, H. *Paramagn. Resonan. Proc. Int. Conf. 1st* **1962**, *2*, 264.
- (13) Bojko, I.; Silebee, R. *J. Magn. Reson.* **1971**, *5*, 339.
- (14) Iwaizumi, M.; Kubota, S.; Isobe, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3227.
- (15) Colburn, C.; Ettinger, R.; Johnson, F. *Inorg. Chem.* **1963**, *2*, 1305.
- (16) Schaafama, T.; Kommandeur, J. *Mol. Phys.* **1967**, *14*, 517.
- (17) Brailsford, J.; Morton, R. *J. Magn. Reson.* **1969**, *1*, 575.
- (18) Pietrzak, T.; Wood, E. *J. Chem. Phys.* **1970**, *53*, 2454.
- (19) Shiotani, M.; Freed, J. *J. Phys. Chem.* **1981**, *85*, 3873.
- (20) Freed, J. In *Spin Labeling: Theory and Applications*; Berliner, L., Ed.; Academic Press: New York, 1976; Vol. 1.
- (21) Schneider, D.; Freed, J. In *Biological Magnetic Resonance. Vol. 8. Spin Labeling: Theory and Applications*; Berliner, L., Reuben, J., Eds.; Plenum Press: New York, 1989.
- (22) Schwartz, R.; Clark, M.; Chamulitrat, W.; Kevan, L. *J. Appl. Phys.* **1986**, *9*, 59.
- (23) Nagata, M.; Yahiro, H.; Shiotani, M.; Lindgren, M.; Lund, A. *Chem. Phys. Lett.* **1996**, *256*, 27.
- (24) Yahiro, H.; Nagata, M.; Shiotani, M.; Lindgren, M.; Li, H.; Lund, A. *Nukleonika* **1997**, *42* (2), 557.
- (25) Yahiro, H.; Shiotani, M.; Freed, J.; Lindgren, M.; Lund, A. *Stud. Surf. Sci. Catal.* **1995**, *94*, 673.
- (26) Yahiro, H.; Li, H.; Benetis, N.; Lindgren, M.; Lund, A.; Nagata, M.; Shiotani, M. *Proc. Int. Symp. Zeolites Micro. Cryst.* Tokyo, 1997.
- (27) Li, H.; Lund, A.; Lindgren, M.; Sagstuen, E.; Yahiro, H. *Chem. Phys. Lett.* **1997**, *271*, 84.
- (28) Moens, P.; De Volder, P.; Hoogewijs, R.; Callens, F.; Verbeeck, R. *J. Magn. Reson. A* **1993**, *101*, 1–15.
- (29) Lawley, D.; Maxwell, A. *Factor Analysis as a Statistical Method*; Butterworth: London, 1971.
- (30) Lindgren, M.; Svensson, M.; Freskgard, P.; Carlsson, U.; Jonasson, P.; Martensson, L.; Jonsson, B. *Biophys. J.* **1995**, *69*, 202–213.
- (31) Visscher, K.; Hom, M.; Loman, H.; Spoelder, H.; Verberne, J. *Radiat. Phys. Chem.* **1988**, *32*, 465.
- (32) Barnes, J.; Bernhard, W. *Radiat. Res.* **1995**, *143*, 85.
- (33) Malinowsky, E.; Howerly, D. *Factor Analysis in Chemistry*; Wiley: New York, 1980.
- (34) Wadsworth, H., Ed. *Handbook of Statistical Methods for Engineers and Scientists*; McGraw-Hill: New York, 1990.
- (35) Budil, D.; Sanghyuk, L.; Saxena, S.; Freed, J. *J. Magn. Reson. Series A* **1996**, *120* (2), 155.
- (36) Fukunaga, K. *Introduction to Statistical Pattern Recognition*; Academic Press: New York, 1990.
- (37) Bao Liu, S.; Barthomeuf, D. *Appl. Catal. A* **1995**, *124*, 81.
- (38) Seidel, A.; Boddenberg, B. *Z. Naturforsch.* **1995**, *50*, 199.
- (39) Lasperas, M.; Cambon, H.; Brunel, D.; Rodriguez, I.; Geneste, P. *Microporous Mater.* **1996**, *7*, 61.
- (40) Williams, C. *Diffusion in Gases and Porous Media*; Plenum Press: New York, 1980.