



Interaction of N₂O with Ag⁺ ion-exchanged zeolites: an FT-IR spectroscopy and quantum chemical ab initio and DFT studies

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Abstract

FT-IR spectroscopy and theoretical ab initio as well as density functional (DFT) methods have been applied to the investigation of the interaction of N₂O with Ag⁺ counter-cations in a ZSM-5 zeolite. As a preliminary part of the study, the adsorption of N₂O on the parent H-Na-ZSM-5 zeolite (from which the Ag-ZSM-5 system was obtained by ion exchange) and the adsorption of CO at low temperature on Ag-ZSM-5, in order to monitor the dispersion of the Ag⁺ ions, were also performed. It was observed that N₂O could be adsorbed on Ag⁺ counter-cations both N-end and O-end down. The two forms produce distinct bands due to the ν_{NN} mode, clearly observable in the 2300–2200 cm⁻¹ range. Conversely, only the ν_{NO} band due to the N-end down adduct was observed at 1325 cm⁻¹, the component corresponding to the O-end down form falling below the low frequency limit of IR transparency of the system. Interestingly, the band due to the ν_{NN} mode of N₂O molecules O-end down adsorbed on Ag⁺ ions appeared coincident with that of N₂O in interaction with Al–OH and ≡Si–OH–Al≡ groups left in the zeolite after exchange with Ag⁺. However, the former N₂O adducts on silver cations appeared to be slightly more stable (less reversible) than the latter adducts.

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1. Introduction

Nitrous oxide (N₂O), has been recognized as an environmental pollutant, and it has also been identified as a greenhouse gas [1]. Its level in the atmosphere continues to increase at a rate of about 0.2% per year,

and this increase has been attributed mainly to anthropogenic activities, in particular to flue gases emitted by stationary and mobile sources such as lean-burn automobiles, coal-fired power plants, electric power generators, nitric acid factories, biomass burning, etc. [1–4]. Several studies devoted to the development of practical catalytic approaches towards the elimination of N₂O emissions have been carried out, and a relevant part of them focused on the use of copper containing catalysts [5,6].

Recently, it was found that the Ag⁺ ion-exchanged zeolites display much higher activity and selectivity compared to widely used Cu⁺ ion-exchanged ZSM-5 zeolites towards the direct photocatalytic decomposition of NO into N₂ and O₂, as well as in the

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selective photocatalytic reduction of NO_x (nitrogen oxides) with ammonia or with hydrocarbons in the presence of excess amounts of oxygen [7–10].

Both Cu^+ and Ag^+ ions have similar $d^{10}s^0$ electronic structures, and they differ only in the principal quantum number for the fully occupied d-shells. Insights on the reasons for their different catalytic abilities were provided by quantum chemical studies on the structural and adsorptive features of these cations in zeolites. Hartree–Fock (HF) and correlated second-order Møller–Plesset perturbation (MP2) calculations indicated highly dispersed Ag^+ counter-ions establish a two-fold coordination to the lattice oxygen atoms that lie much lower in energy than the three-coordinated state both at the HF and MP2 levels of theories [11,12]. The mono-coordination state was found to be unstable since it can be easily transformed into the two-coordinated state without any barrier. The comparison of the adsorption energies of N_2O and NO estimated at the MP2 level for the Cu^+ and Ag^+ ion-exchanged zeolites have showed that both molecules bind relatively strongly to the former catalyst. These results indicate that the higher adsorption ability of N_2O and NO on Cu^+ may be the reason for their decreased mobility on the catalytic sites, thus leading to a decrease in the formation of reaction products.

In this work we put some steps forwards in the elucidation of the interaction of nitrous oxide with Ag^+ sites in ZSM-5, which can occur through the N-end and/or the O-end down adsorption of N_2O molecules, by combining the experimental data obtained with IR spectroscopy with the results of *ab initio* as well as density functional (DFT) calculations, also with the aim to provide a more definite assignment of the spectral bands observed experimentally. This aspect may be of a general interest, as IR spectroscopy is among the most widely employed experimental methods used in the investigations of heterogeneous catalysts with probe and/or reactant molecules.

2. Experimental

2.1. Materials and experimental method

H-Na-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.8$), containing H^+ and Na^+ in a ca. 1:1 ratio as counter-cations, was

used as starting material. From this parent zeolite, Ag-ZSM-5 sample was prepared by a conventional ion-exchange technique using 5.0×10^{-3} M AgNO_3 solution under stirring at room temperature for 24 h. After filtration, the powder was dried at 373 K overnight and then calcined in air at 723 K for 4 h. Atomic absorption analysis indicated that the Ag^+ loading was 6.1 wt.%, which corresponds to a 45% exchange level. A Na-ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 23.8$) was also employed for some reference spectroscopic experiments. For the adsorption experiments, high purity CO and N_2O (Takachiho Chemical Co.) were employed.

For the IR experiments, the samples, in the form of a self-supporting pellet, were placed in home-made quartz cells allowing measurements at room temperature or at ca. 100 K, permanently connected to a vacuum line (residual pressure: 1×10^{-6} Torr, where 1 Torr = 133.33 Pa) allowing all thermal treatments and adsorption–desorption experiments to be carried out *in situ*. The spectra were recorded with a Jasco FT-IR 660 at resolution 2 cm^{-1} . Before the adsorption experiments, the samples were re-treated in the IR cell by heating in 10 Torr O_2 at 723 K for 1 h and then outgassing at 473 K for 1 h.

2.2. Calculation method and cluster models

Ab initio and DFT molecular orbital calculations were performed using the Gaussian 94 program package [13]. Two cluster models were applied to represent the structural properties of the Ag^+ ion-exchanged zeolites. The smallest 1T model is comprised of one AlO_4 tetrahedron in which H atoms were used to saturate the dangling bonds and to account for the boundary effects [14,15]. The extra one negative charge of AlO_4 tetrahedron was compensated by Ag^+ to achieve electroneutrality. In the extended 3T model, the central AlO_4 tetrahedron is linked (by shared corners) to two other SiO_4 tetrahedra. The dangling bonds were also saturated with H atoms. Again, the negative lattice charge arising from the presence of the AlO_4 tetrahedron were compensated by adding one Ag^+ . The positions of the terminal H atoms were fixed while the coordinates of rest other atoms and the charge balancing Ag^+ counter-metal ion have been fully optimized.

Geometry optimizations of the initial cluster models as well as the adsorption complexes of the N_2O

molecules were carried out at the HF and DFT levels of theory using two combined basis sets and followed by frequency calculations. In the first combined basis sets denoted as CBS1, standard double-zeta quality Lanl2dz basis sets were applied to all hydrogen, aluminum, silicon and silver atoms while other oxygen and nitrogen atoms were described by 6-31G** basis sets. The former Lanl2dz basis sets are those of well-known Los Alamos National Laboratory (LANL) developed effective core potentials plus double-zeta basis sets for all valence electrons [16–18]. In the second combined basis sets denoted as CBS2, full 6-311++G(2d,2p) basis sets were applied to all oxygen and nitrogen atoms, while the H, Al, Si, and Ag centers were described with the Lanl2dz basis sets. In addition, geometries of adsorption complexes of N₂O were optimized at the DFT level using only Lanl2dz basis sets. DFT calculations were performed using the Becke's three-parameter hybrid method with the Lee, Yang and Parr (B3LYP) gradient-corrected correlation functional [19,20].

3. Results and discussion

3.1. IR data

3.1.1. N₂O adsorption on the parent H-Na-ZSM-5

Fig. 1A shows the spectra of the parent H-Na-ZSM-5 zeolite in vacuo (curve a) and in the presence of decreasing pressure of N₂O (curves b–f) in the 3800–3100 cm⁻¹ range.

The initial spectrum of the sample exhibited a narrow peak at 3747 cm⁻¹, asymmetric towards the low frequency side due to silanols at defect terminations of the zeolite framework, and two broader bands at 3663 and 3615 cm⁻¹, assigned to the O–H stretching mode of Al–OH groups in defective (internal or external) positions and to structural bridged ≡Si–OH–Al≡ groups, respectively [21]. The admission of 10 Torr N₂O at room temperature did not affect the band at 3747 cm⁻¹, indicating that in this condition silanols do not interact with N₂O, while it resulted in a slight decrease in intensity of the bands at 3663 and 3615 cm⁻¹, accompanied by the appearance of a broad adsorption in the 3600–3200 cm⁻¹ range (Fig. 1A, b). Such behaviour indicates that a small fraction of the Al–OH and bridged ≡Si–OH–Al≡

groups act as adsorbing centers for N₂O molecules, with a consequent shift of their stretching band to lower frequency, as well known [22]. Furthermore, $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$ combination of bands (these characteristic ν_3 , ν_2 , and ν_1 modes correspond to the NN stretching, NNO bending and NO stretching vibrations, respectively [23])⁴ of adsorbed N₂O molecules can also contribute to the broad features in the 3600–3200 cm⁻¹ regions. The limited extent of the perturbation of the 3663 and 3615 cm⁻¹ accounts for the expected weak energy of interaction of N₂O with the hydroxyl centers responsible for those bands. The effect of such perturbation progressively decreased by decreasing the N₂O pressure (Fig. 1A, c–e), and the original spectrum was fully restored after briefly outgassing at room temperature (Fig. 1A, f).

At lower frequency, the admission of N₂O resulted in the appearance of a complex band with a main peak at 2227 cm⁻¹, a weaker maximum at 2237 cm⁻¹ and a shoulder at 2248 cm⁻¹ (Fig. 1B, a), which are in the range where bands due to the ν_3 of adsorbed N₂O molecules are expected [24]. It must be noted that, for the sake of clarity, in this region the spectra of adsorbed N₂O are reported after subtraction of the spectrum of the sample in vacuo as background. Parallel experiments of N₂O adsorption on fully Na-ZSM-5 zeolites (not reported) allowed us to conclude that the component at 2237 cm⁻¹ is due to N₂O molecules adsorbed on Na⁺ cations in the H-Na-ZSM-5 used. The most intense band at 2227 cm⁻¹ should be then due to N₂O molecules in interactions with Al–OH and to bridged ≡Si–OH–Al≡ groups. Finally, the shoulder at 2248 cm⁻¹ may correspond to N₂O molecules adsorbed on some other defect sites and/or some other adsorption forms (this minor feature will be discussed in more detail in a next paper), while the weak, broad tails on both the high and low frequency side of the main absorptions may be assigned to hindered rotation modes of N₂O molecules within the zeolitic channels. The three components at 2227, 2237, and 2248 cm⁻¹ decrease in intensity by decreasing the N₂O pressure,

⁴ We adopted Nakamotos's notation as his book is mostly used by inorganic and coordination chemists. Herzberg used a reverse numbering for the two Σ^+ modes (ν_1 and ν_3), but the two notations are perfectly equivalent, in view of the non-centro-symmetric structure of N₂O.

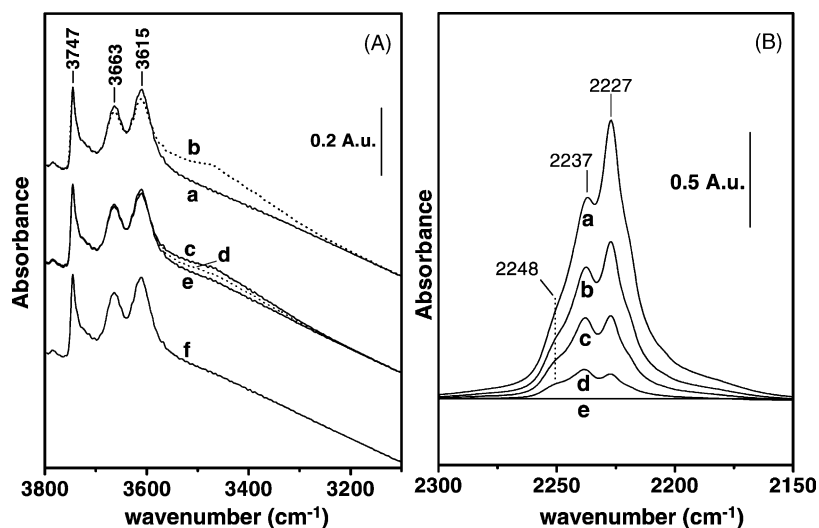


Fig. 1. IR spectra of N_2O adsorbed on H-Na-ZSM-5 at room temperature. (A) Spectra in the $3800\text{--}3100\text{ cm}^{-1}$ region of the sample: (a) in vacuo, and in the presence of (b) 10, (c) 6, (d) 3, (e) 1 Torr N_2O , and (f) after 1 min outgassing at room temperature. (B) Spectra in the $2290\text{--}2115\text{ cm}^{-1}$ range of the sample under decreasing pressure of N_2O , from which the spectrum of the sample before the admission of N_2O as background has been subtracted: (a) 10, (b) 6, (c) 3, (d) 1 Torr N_2O , and (e) after 1 min outgassing at room temperature.

and disappeared after briefly outgassing at room temperature (Fig. 1B, b–e).

No bands due to the ν_1 mode of adsorbed N_2O , expected to occur at frequency lower than 1380 cm^{-1} [24], were detected, indicating that they should occur below the low frequency limit of IR transparency of the zeolite (ca. 1280 cm^{-1}).

3.1.2. CO adsorbed at low temperature on Ag-ZSM-5

IR spectroscopy of the CO adsorption at ca. 100 K is used as a preliminary step before the spectroscopic investigation of the interaction of N_2O with Ag-ZSM-5 derived from the parent H-Na-ZSM-5 zeolite.

The spectrum of the Ag-ZSM-5 zeolite in the $3800\text{--}3100\text{ cm}^{-1}$ range (Fig. 2A, a) did not appear significantly different from that of the parent H-Na-ZSM-5 (see Fig. 1A, a), indicating that Ag^+ mainly replaced Na^+ ions. The admission of CO (10 Torr) left essentially unperturbed the band due to silanols, whereas resulted in the almost complete disappearance of the 3663 and 3615 cm^{-1} bands, which are transformed into two broad components at 3500 and 3325 cm^{-1} (Fig. 2A, b). The latter are due to Al-OH and $\equiv\text{Si-OH-Al}\equiv$ hydrogen bonded with CO [22]. By decreasing the CO pressure, the 3550 and 3325 cm^{-1} bands progressively faded away

and the 3663 and 3615 cm^{-1} ones were progressively restored (Fig. 2A, c–e), and under 0.01 Torr CO the initial spectral profile was fully restored (Fig. 2A, f).

For the sake of simplicity the spectra of adsorbed CO in the ν_{CO} region are shown after subtraction of the spectrum of the sample in vacuo as background. At high CO coverage a complex band at 2186 cm^{-1} with an evident shoulder at 2190 cm^{-1} and two weaker, partially resolved components at 2175 and 2165 cm^{-1} are present (Fig. 2B, a). These two latter components can be assigned to CO adsorbed on unexchanged Na^+ [25] and protons [26], respectively. Such adducts are poorly stable, and the bands they produced completely disappeared by decreasing the CO pressure (Fig. 2B, b–g).

On the basis of previous studies on Ag-ZSM-5 zeolites [27,28], the maximum at 2186 cm^{-1} and the shoulder at 2190 cm^{-1} can be assigned to the symmetric and antisymmetric modes of $\text{Ag}^+(\text{CO})_2$ species formed on highly coordinatively unsaturated Ag^+ ions. By decreasing the CO coverage, these two components are progressively converted into a single band at 2192 cm^{-1} , due to $\text{Ag}^+(\text{CO})$ monocarbonyl species (Fig. 2B, b–g). These features clearly indicate that the Ag-ZSM-5 contained isolated Ag^+ centers, and that the activation procedure employed did not

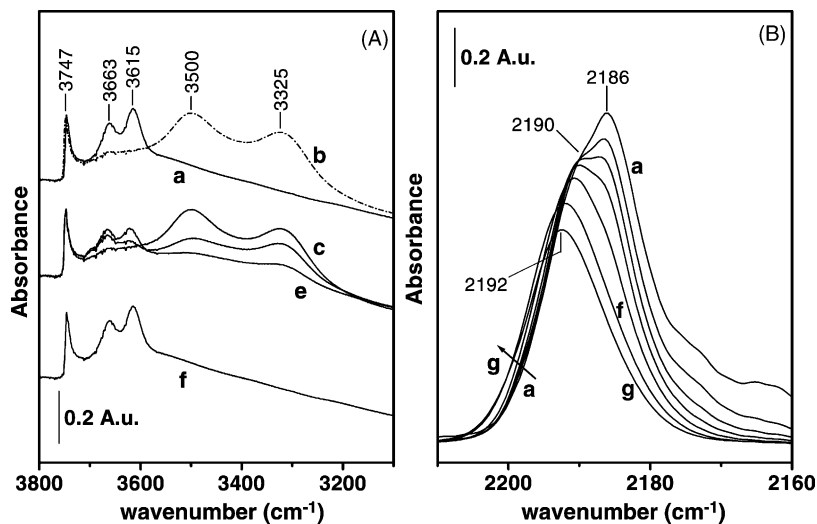


Fig. 2. IR spectra of CO adsorbed on Ag-ZSM-5 at ca. 100 K. (A) Spectra in the 3800–3100 cm⁻¹ region of the sample: (a) in vacuo, and (b–f) in the presence of decreasing pressure of CO from 10 to 0.01 Torr CO. (B) Spectra in the 2220–2160 cm⁻¹ range of the sample under decreasing pressure of CO, from which the spectrum of the sample before the admission of CO as background has been subtracted: (a–f) from 10 to 0.01 Torr CO, and (g) after 15 min outgassing at ca. 100 K.

result in the formation of any Ag^o whose band are expected at ca. 2060 cm⁻¹ [29].

3.1.3. N₂O adsorption on Ag-ZSM-5

In a subsequent experiment, N₂O was dosed at room temperature on Ag-ZSM-5. The most relevant

IR features observed when N₂O was adsorbed on the Ag-ZSM-5 sample are shown in Fig. 3 (spectra reported after subtraction of the spectrum of the sample before admission of N₂O as background). In the ν₃ mode region, a main band at 2256 cm⁻¹, with a shoulder at ca. 2248 cm⁻¹, and a peak at 2227 cm⁻¹

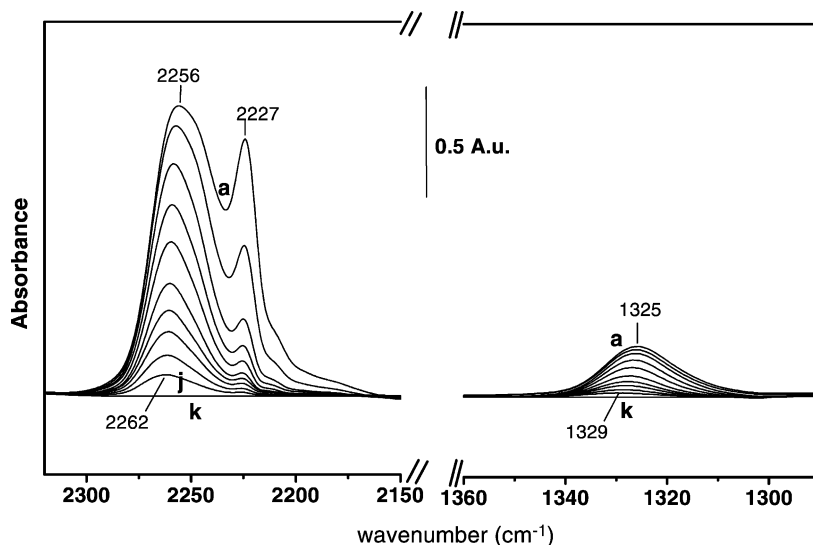


Fig. 3. IR spectra of N₂O adsorbed on Ag-ZSM-5 at room temperature. (a–j) Curves correspond to decreasing equilibrium pressure from 10 to 0.1 Torr N₂O and (k) after 1 min outgassing at room temperature.

were observed, while in the ν_1 mode region a weaker band at 1325 cm^{-1} , also slightly asymmetric towards the low frequency side, appeared (Fig. 3, a).

The peak at 2227 cm^{-1} appears similar to that already observed for the parent H-Na-ZSM-5, due to the N_2O interaction with Al–OH and $\equiv\text{Si}-\text{OH}-\text{Al}\equiv$ groups. Still in comparison with the parent zeolite, the absence of a defined component at 2237 cm^{-1} in the spectrum of N_2O adsorbed on Ag-ZSM-5 confirmed that most part of Na^+ ions have been exchanged for Ag^+ . The 2256 and 1325 cm^{-1} components appear as specific features of the Ag-ZSM-5 in interaction with N_2O , and should be then ascribed to $\text{Ag}^+ \cdots \text{N}_2\text{O}$ adducts. A detailed assignment of these bands will be discussed in the following, on the basis of the results of the theoretical calculations. On the other hand, the assignment of the shoulder at 2248 cm^{-1} , similar in position to a minor component observed also by dosing N_2O on the parent H-Na-ZSM-5, is difficult at present.

Some other spectral features when the N_2O coverage is decreased (Fig. 3, b–k) should be noted: (i) the shoulder at 2248 cm^{-1} as well as main part of the peak at 2227 cm^{-1} disappear more quickly (Fig. 3, a–d) than the bands at 2256 and 1325 cm^{-1} , indicating that some of N_2O adducts formed are less stable; however, the small fraction of the band at 2227 cm^{-1} left at lower N_2O coverage seems to decrease in intensity simultaneously with the 2256 and 1325 cm^{-1} components (Fig. 3, e–k); (ii) the intensity of these two components changes in a parallel way in all the range of N_2O pressure, suggesting that they are produced by the same type of N_2O adducts; (iii) these two bands progressively shift to 2262 and 1329 cm^{-1} , respectively, and as was also suggested by the spectra of adsorbed CO, it can be assumed that Ag^+ sites are well dispersed and isolated. This behaviour cannot be ascribed to some interactions between the adsorbed molecules, but may indicate some heterogeneity in the Ag^+ ions exposed within the zeolite channel.

3.2. Theoretical data

Since the energetic and geometrical changes that take place during the adsorption process of NO and N_2O on Ag^+ ion-exchanged zeolites have been considered elsewhere [11,12] at the HF and MP2 levels by applying 1T, 3T and 6T cluster models, here atten-

Table 1

Geometries (bond distance, A–B, in Å and tilt angle, φ , in degree) and adsorption energies (δE in kcal/mol) of the two adsorption forms of N_2O on Ag^+ ion-exchanged zeolites mimicked by the use of 1T, 3T, and 6T cluster models at the B3LYP/Lan12dz level of the theory

	Cluster model		
	1T	3T	6T
N-end down adsorption form			
$\text{O}_{\text{lat.}}-\text{Ag}^{\text{a}}$	2.340	2.355	2.365
Ag–N	2.301	2.286	2.268
N–N	1.158	1.157	1.157
N–O	1.231	1.231	1.230
φ^{b}	179.8	169.8	156.3
δE^{c}	7.7	7.8	8.1
O-end down adsorption form			
$\text{O}_{\text{lat.}}-\text{Ag}^{\text{a}}$	2.343	2.364	2.371
Ag–O	2.431	2.431	2.405
N–N	1.247	1.245	1.246
N–O	1.156	1.156	1.155
φ^{b}	136.4	132.1	132.6
δE^{c}	5.9	6.1	6.5

^a The $\text{O}_{\text{lat.}}$ stands for lattice oxygen. In all cluster models, Ag^+ tends to have two bonds with the lattice oxygen atoms.

^b This tilt angle is formed by the axis of N_2O and Al–Ag.

^c Corrected for BSSE.

tion is directly paid to the clarification of the origin of bands that appeared during the adsorption of N_2O on the target catalyst surface. Nevertheless, let us briefly point out some common features, both for the above HF method as well as the MP2 [11,12] and B3LYP methods. The results of the latter B3LYP calculations are presented in Table 1, which is based on the use of the above 1T, 3T and 6T cluster models (Figs. 4 and 5). Note that the adsorption energies (δE) were calculated as the total energy difference between the adsorption complex and the sum of the isolated initial cluster and adsorbate molecule. These energies were corrected for basis set superposition errors (BSSE) by using the full Boys–Bernardi counterpoise correction scheme [30–32].

First of all, the smallest 1T cluster model covers only part of the largest 6T one, and is associated with the AlO_4 tetrahedron and the Ag^+ counter-ion. At the same time, the intermediate 3T cluster model takes the effects of the next-neighbor two SiO_4 tetrahedra into account as compared to that of the minimal 1T cluster model (Figs. 4 and 5). As the cluster model

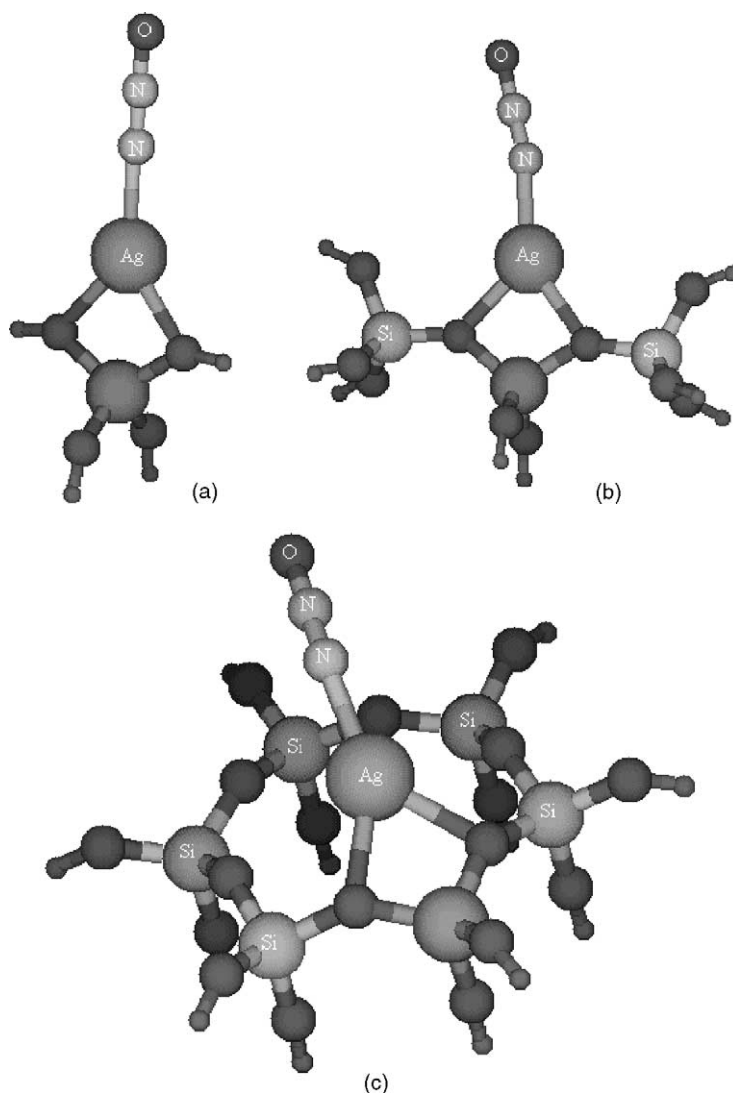


Fig. 4. The optimized N-end down adsorption complexes of N_2O on Ag^+ ion-exchanged zeolites mimicked by (a) 1T, (b) 3T, and (c) 6T cluster models.

is enlarged, some numerical changes in the bond distances and bond angle have been obtained, while the relative stability in the coordination state of the Ag^+ cation by lattice oxygens remain the same as in the case of the HF or MP2 levels of theories [11,12]. The differences in bond distances are within 0.02 \AA while the MP2 and DFT levels lead to slightly elongated Al–O bonds for the O atoms with which Ag^+ has established bonds as compared to those of the HF level of the theory [11,12]. Second, the interaction be-

tween N_2O and Ag^+ is dominantly electrostatic and local in nature [11,12,33], which is further supported here by the estimated adsorption energies as well as by the optimized structural properties of both the adsorption forms of N_2O on Ag^+ ion-exchanged zeolites (Table 1). Since the estimated adsorption energies (corrected for the BSSE) for the N-end down and O-end down forms of N_2O on Ag^+ ions were found to be quite close to each other, with a difference of only 2.1 and 1.7 kcal/mol in favor of the N-end down form

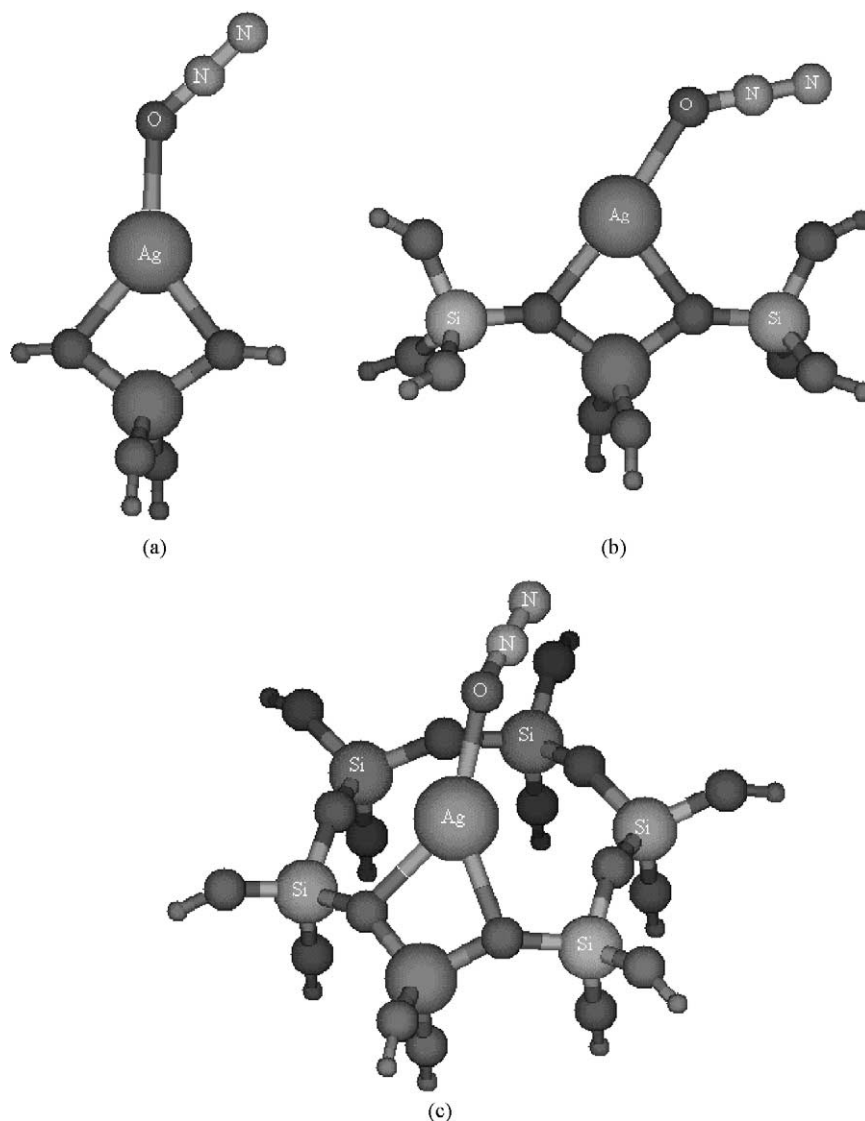


Fig. 5. The optimized O-end down adsorption complexes of N_2O on Ag^+ ion-exchanged zeolites mimicked by (a) 1T, (b) 3T, and (c) 6T cluster models.

estimated at the correlated MP2 [11,12] and B3LYP levels, respectively, one may expect that the superposition of the bands for both the NN and NO stretching modes of N_2O would arise from the presence of both adsorption forms of N_2O on the Ag^+ ion-exchanged zeolites. Also note that the structural properties of the adsorbed N_2O fragment are entirely the same in all the applied cluster models.

Let us now move to our main goal to consider the origin of the bands observed in experiment. The results of the frequency calculations for the interaction of N_2O with Ag^+ ions hosted in the zeolite sites, based on the use of two different basis sets and two distinct cluster models, are listed in Table 2. The reduced stretching modes for the NN and NO vibrations (ν_3 and ν_1 , respectively) in those adsorption

Table 2

The calculated ν_{NN} (ν_3) and ν_{NO} (ν_1) stretching vibration frequencies estimated at the HF and B3LYP levels of the theory^a

Basis set		RHF		B3LYP	
		ν_{NN}	ν_{NO}	ν_{NN}	ν_{NO}
1T-CBS1 ^b	N-end down	2233	1349	2265	1320
	O-end down	2265	1280	2231	1257
3T-CBS1 ^b	N-end down	2236	1344	2269	1322
	O-end down	2260	1268	2229	1252
1T-CBS2 ^c	N-end down	2227	1344	2268	1320
	O-end down	2261	1271	2238	1255

^a Numbers in each column corresponds to the N-end down and O-end down adsorption forms of N_2O on Ag^+ zeolite counter-cations, respectively.

^b Lan12dz basis sets for Al, Ag, and hydrogen atoms, and 6-31G** for O and N atoms. 1T and 3T correspond to the minimal and extended cluster models used, respectively.

^c Lan12dz basis sets for Al, Ag and hydrogen atoms, and 6-311++G(2d,2p) for O and N atoms.

complexes were estimated by the use of a scaling factor [34–37] which is obtained from an optimal conformity of the calculated and the observed frequencies for the gas phase N_2O [24]. For the latter gas phase N_2O , ν_3 and ν_1 are equal to 2224 and 1285 cm^{-1} , respectively [24]. The ν_3 and ν_1 vibrations of N_2O in either N-end down or O-end down adsorption forms were found to be less dependent both on the basis sets applied, and on the size of cluster models used. For both ν_3 and ν_1 vibrations considered, the differences were within 5–10 cm^{-1} when compared at the distinct level of the theories. Note, however, the absolute values of ν_3 and ν_1 vibrations without the use of scaling factors are quite sensitive to the basis set applied and, to a lesser extent, on the cluster model used, as can be highly expected [34–37]. It should be also noted that this conclusion is true for all-electron calculations and not for the cases when the core electrons are replaced by the effective core potentials for the adsorbed molecule(s) [11,12] for which the estimated frequencies were found to be less accurate.

Both methods applied produced values for the position of the IR bands of adsorbed N_2O in a qualitative agreement with the experimental data. As for their assignment, they allowed us to conclude that the experimental band at 1325 cm^{-1} is due to the ν_1 mode of N_2O molecules N-end down adsorbed on Ag^+ . Conversely, a contrasting indication on the nature of the

experimental band at 2256 cm^{-1} is provided by different methods. B3LYP calculations predicted that this band should be due to N_2O molecules adsorbed N-end down on Ag^+ , while HF results indicate the O-end down adsorption. Perhaps, this is associated with the fact that the RHF level overestimates the stability of the O-end down adsorption of N_2O over the N-end down one due to the lack of electron correlation effects [11,12]. However, calculations (details not reported for the sake of brevity) indicated that the intensity of the ν_3 band should be about four to five times as large as that of the ν_1 one, in good agreement with the observed IR data. Interestingly, both calculations also indicate that the ν_3 mode of N_2O interacting with the Ag^+ sites may produce a band not so different in position from the experimentally observed band at 2227 cm^{-1} , also attributable to N_2O molecules adsorbed on Al–OH and $\equiv\text{Si}-\text{OH}-\text{Al}\equiv$ groups present in the Ag-ZSM-5 sample, almost in the same amount as in the parent H-Na-ZSM-5 zeolite (see above). The latter result reinforces the idea that the experimental band at 2227 cm^{-1} in the spectra of N_2O adsorbed on Ag-ZSM-5 (Fig. 3), which exhibit almost the same intensity as that in the spectra of N_2O interacting with H-Na-ZSM-5 (Fig. 1), may be due in part to the second adsorption form of $\text{N}_2\text{O}\cdots\text{Ag}^+$ adducts. It can be also proposed that the less reversible fraction of the band at 2227 cm^{-1} could be due to a less favorable form of the adsorbed species, which exhibited an evolution under decreasing N_2O pressure parallel to that of the 2256 and 1325 cm^{-1} components (see Fig. 3, e–k).

4. Conclusions

The interaction of N_2O with the Ag^+ ion-exchanged zeolite at an exchange level of 45% shows complex FT-IR spectra features. The spectrum in the 3800–3100 cm^{-1} ranges did not appear significantly different from that of the parent H-Na-ZSM-5 zeolite indicating that Ag^+ mainly replaced the Na^+ ones. The admission of N_2O left essentially unperturbed the band centered at 3747 cm^{-1} due to the surface silanol groups, while it resulted in a slight decrease in intensity of the bands at 3663 and 3615 cm^{-1} .

N_2O can interact with Ag^+ centers in both the N-end and O-end down forms producing a superpo-

sition of peculiar ν_3 and ν_1 IR bands. According to DFT calculations, main ν_3 and weaker ν_1 modes of the N-end down form can be clearly observed in the experimental spectra, centered at 2256 and 1325 cm^{-1} (high N_2O coverage), respectively. As for IR absorptions due to the O-end down interaction of N_2O molecules with Ag^+ ions, the ν_1 band, predicted by calculations, fall in the 1280–1250 cm^{-1} ranges. However, it was not observable, because located below the low frequency limit of the IR transparency of the zeolite.

In the experimental spectra, the ν_3 band at 2227 cm^{-1} appeared coincident with the component due to N_2O adsorbed on Al–OH and $\equiv\text{Si}-\text{OH}-\text{Al}\equiv$ groups, still present in the materials, but can be distinguished at low N_2O coverage, because of its lower reversibility.

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