The complex NO⁺·H₂S, which is assumed to be an intermediate in acid rain formation, exhibits thermodynamic stability of $\Delta H_{298}^\circ = -76$ kJ mol⁻¹, or $\Delta G_{298}^\circ = -47$ kJ mol⁻¹. Its further transformation via H-transfer is associated with rather high barriers. One of the conceivable routes to lower the energy of the transition state is the action of additional solvent molecule(s) that can mediate proton transfer. We have studied several NO⁺·H₂S structures with one or two additional water molecule(s) and have found stable structures (local minima), intermediates and saddle points for the three-body NO⁺·H₂S·H₂O and four-body NO⁺·H₂S·(H₂O)₂ clusters. The hydrogen bonds network in the four-body cluster plays a crucial role in its conversion to thionitrous acid.

**Keywords**: Hydrogen bond; Hydration; Nitric oxide cation; Hydrogen sulfide; Quantum chemistry.

The formation of ion clusters and ion-molecule complexes plays an important role in many branches of physics, chemistry and biology because these processes are relevant to gas-phase solvation, acid-base equilibria, combustion, catalysis and atmospheric phenomena. They often include various types of intermolecular interactions which can become the initial step of chemical reaction. Of particular interest among them are those ion-molecule interactions that are part of important gas-phase solvation processes in the stratosphere (altitudes 15-50 km) and ionosphere (altitudes above 50 km).

Quite a few studies of ion-molecule reactions have been focused on the clustering phenomena related to nitrogen oxides which may exist in the upper Earth atmosphere. Nitrogen oxides enter into an important part of the atmospheric chemical reactivity. From the environmental point of
view, the most abundant are N_2O, NO and NO_2, collectively denoted as the N_xO_y family. They are produced by photochemical processes (from molecular nitrogen and oxygen) during lightning and due to anthropogenic activity.

Nitric oxide is the parent molecule for the ionic species NO^+. The nitric oxide cation is one of the major ionic constituents of the ionosphere in the D- (altitudes 50–90 km), E- (altitudes 90–140 km) and F-layers (above 140 km). In the D-layer, also ion O_2^+ and traces of Mg^+, Fe^+, Na^+, K^+ and Cs^+ were observed. NO^+ has an impact on both ion-molecule chemistry and physics of the atmosphere since it is quite abundant and can influence not only numerous chemical processes but also physical properties of the atmosphere, such as electric conductivity. Concentration of this ion in higher layers of the ionosphere, E and F, is lower due to recombination with free electrons. NO^+ is produced either directly by day-time photo-ionization of nitric oxide by solar Lyman-α radiation (λ ~120 nm)

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]

\[ \text{NO} + h\nu \rightarrow \text{NO}^+ + e \]

or indirectly, from N_2 and O_2 ionized by X-rays:

\[ \text{O}^+ (^4S) + \text{N}_2 \rightarrow \text{NO}^+ (X^1\Sigma^+) + \text{N} (^4S) \]

\[ \text{N}_2^+ (A^2\Pi) + \text{NO} \rightarrow \text{N}_2 (X^1\Sigma^+) + \text{NO}^+ (X^1\Sigma^+) \].

Molecular ions present in the D-region can react with water vapour to produce water cluster ions, gravitationally penetrate through the border between ionosphere and stratosphere and participate in clustering reactions with other atmospheric molecules originating from natural or industrial sources. The key step in these processes, atmospheric clustering of NO^+ with water, received considerable attention in the last three decades, as reflected by numerous experimental and theoretical studies and reviews.

The NO^+H_2O ion-molecule complex has been suggested as a key intermediate in the production of various hydronium-water complexes, but the efficient formation of this particular complex in the atmosphere is believed to depend strongly on the presence and abundance of the related complexes NO^+X (where X is O_2, N_2, CO_2). The atmospheric conversion process can include as the first step the formation of a complex between NO^+ and molecule X, followed by rapid exchange reaction. For example, for X = CO_2
Dunkin et al.\textsuperscript{21} have proposed the sequence with the participation of a third particle

\begin{align*}
\text{NO}^+ + \text{CO}_2 + \text{M} & \rightarrow \text{NO}^+ \text{CO}_2 + \text{M} \\
\text{NO}^+ \text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{NO}^+ \text{H}_2\text{O} + \text{CO}_2 .
\end{align*}

The importance of NO\textsuperscript{+} in atmospheric chemistry can be illustrated by its relation to H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} clusters. Water cluster ions H\textsuperscript{+}H\textsubscript{2}O and H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{2} have been found to dominate the D-region around the altitude 80 km and can affect both clustering and exchange reactions of NO\textsuperscript{+} with a variety of neutral ligands (N\textsubscript{2}, CO\textsubscript{2}). On the basis of the flowing-afterglow experiments performed by Fehsenfeld and Ferguson\textsuperscript{10,21} as well as by Lineberger and Puckett\textsuperscript{22}, it was suggested that the formation of cluster ions H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} can proceed from NO\textsuperscript{+}H\textsubscript{2}O in a multistep hydration\textsuperscript{10,22,23} mechanism

\begin{align*}
\text{NO}^+\text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{NO}^+\text{(H}_2\text{O})_2 \\
\text{NO}^+\text{(H}_2\text{O})_2 + \text{H}_2\text{O} & \rightarrow \text{NO}^+\text{(H}_2\text{O})_3 \\
\text{NO}^+\text{(H}_2\text{O})_3 + \text{H}_2\text{O} & \rightarrow \text{HONO} + \text{H}^+\text{(H}_2\text{O})_3 .
\end{align*}

H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} clusters with even higher n imply the production of HNO\textsubscript{3} in the upper atmosphere\textsuperscript{10}. Thus, NO\textsuperscript{+} is indirectly participating in acid rain formation. These findings were confirmed by pulsed high-pressure ion source mass spectroscopy\textsuperscript{24} and vibrational predissociation laser spectroscopy supported by ab initio calculations\textsuperscript{19}.

Less is known about the interactions of NO\textsuperscript{+} with the other conceivable neutral ligands which can be present at the border between stratosphere and ionosphere as a consequence of industrial production or volcanic activity. Among them, CH\textsubscript{3}CN, NH\textsubscript{3}, CH\textsubscript{4}, CH\textsubscript{3}OH, HCN, SO\textsubscript{2}, HSO\textsubscript{3} (refs\textsuperscript{13,14,25}) were mentioned in the literature. These molecules can collide with NO\textsuperscript{+} and form transient structures that, in principle, can either affect NO\textsuperscript{+} clustering and subsequent ion-molecule chemistry or can form aerosols. Arijs has stressed the importance of the knowledge of stratospheric ion composition and ion-molecule interactions because it can lead to the detection of trace gases so far unknown\textsuperscript{14}. One example of such complexes can be NO\textsuperscript{+}H\textsubscript{2}S. In regions with strong air pollution or increased volcanic activity hydrogen sulfide or other gases can persist at elevated partial pressure and contribute to NO\textsuperscript{+} clustering. A key issue related to the clustering of the NO\textsuperscript{+}H\textsubscript{2}S complex with water molecules is the problem of the proton trans-
fer under “wet” conditions leading to thionitrous acid (HSNO). Recently, we have published a pilot study of the potential energy surface of this complex using ab initio methods investigating thermodynamic stability of various isomers of NO⁺·H₂S and the structural features of their model harmonic IR spectra. Our calculations implied no proton transfer in the NO⁺·H₂S system under dry conditions because of unacceptably high energy barriers associated with this process.

One of the conceivable routes to lower the energy of the transition state is the assistance of additional solvent molecule(s) which can mediate the proton transfer. The aim of this paper is to investigate the possibility of the conversion of water-clustered NO⁺·H₂S into HSNO via proton-transfer reaction and the role of water molecules in this mechanism.

METHODS

In this study, we have limited our investigations of NO⁺ clustering to two types of complexes: the three-body cluster NO⁺·H₂S·H₂O and the four-body cluster NO⁺·H₂S·(H₂O)₂. For the geometry optimizations of the three-body cluster we have used DFT-BLYP, DFT-B3LYP and MP2 methods with correlation-consistent basis set of triple-zeta quality (cc-pVTZ), while only the MP2/cc-pVTZ method was used for the four-body cluster. For the three-body cluster we have selected the BLYP and B3LYP functionals to check their performance against the MP2 method because we plan to use DFT for modelling of larger clusters. Harmonic frequencies of each structure were calculated to confirm the nature of the stationary point. For both types of complexes we have also evaluated single-point energies at the CCSD(T) level using cc-pVTZ basis set at MP2/cc-pVTZ optimal geometries to obtain final reaction profiles. For the CCSD(T) energy profile (ΔH and ΔG values) we have used MP2 frequencies in thermochemistry calculations.

We have also checked the basis set superposition error (BSSE) for the cc-pVTZ basis set for the cases where the geometry changes accompanying the cluster formation were negligible. This was possible in evaluating the interaction energy of three models: NO⁺·H₂S + H₂O, NO⁺·H₂O + H₂S and NO⁺·H₂S·H₂O + H₂O at the CCSD(T) level. The counterpoise correction (CPC) was applied in the calculations of interaction energies for the resulting clusters. Thermodynamic properties, reaction enthalpies and Gibbs energies, were calculated assuming the ideal gas and rigid-rotor/harmonic oscillator approximation. All calculations were carried out using the Gaussian 03 and ACES-II suites of programs. Ball-and-stick structures were produced using MOLDEN.
RESULTS AND DISCUSSION

The optimized structures for monohydrated NO⁺H₂S are depicted in Figs 1–3. To illustrate the performance of the BLYP, B3LYP and MP2 methods we have shown the values of bond lengths (from top to bottom for each row) in Figs 1–3. For the remaining structures we present only MP2/cc-pVTZ geometry parameters. Reaction profiles for the NO⁺H₂S·H₂O clus-

![Diagram of Local minimum NO⁺H₂O·H₂S (L)](image)

**FIG. 1**
Local minimum NO⁺H₂O·H₂S (L)

![Diagram of Global minimum NO⁺H₂S·H₂O (G)](image)

**FIG. 2**
Global minimum NO⁺H₂S·H₂O (G)
ter are in Figs 4 (ΔH_{298}) and 5 (ΔG_{298}). The optimized structures for bihydrated NO⁺·H₂S are depicted in Figs 6–11. Reaction profiles for the (H₂O)_2·NO⁺·H₂S clusters are depicted in Fig. 12. The MP2/cc-pVTZ Cartesian coordinates of the reactants, products, intermediates and transition states considered in this study are given in Supplementary material.

![Fig. 3](transition_state.png)

**Fig. 3**
Transition state between (L) and (G)

![Fig. 4](enthalpy_profiles.png)

**Fig. 4**
Enthalpy profiles for the cluster H₂O·NO⁺·H₂S: • BLYP, ■ B3LYP, ▲ MP2, ● CCSD(T)
FIG. 5
Gibbs energy profiles for the cluster H₂O·NO⁺·H₂S: ◆ BLYP, ■ B3LYP, ▲ MP2, ● CCSD(T)

FIG. 6
Minimum (H₂O)₂·NO⁺·H₂S (M1)
We have found three stationary points on the NO$^+$·H$_2$S·H$_2$O potential energy surface: local minimum, global minimum and transition state. The local minimum corresponds to the sequential structure NO$^+$H$_2$O·H$_2$S (Fig. 1) that can be regarded as a complex NO$^+$H$_2$O solvated by a H$_2$S molecule. In

**Fig. 7**
Minimum (H$_2$O)$_2$·NO$^+$·H$_2$S (M2)

**Fig. 8**
Quasi-symmetrical minimum H$_2$O·NO$^+$·H$_2$S·H$_2$O (M3)
**FIG. 9**
Transition state 1 for the proton transfer (TS1)

**FIG. 10**
Transition state 2 for the proton transfer (TS2)
the global minimum (Fig. 2) the roles of ligands are reversed and the structure can be regarded as a distorted three-membered ring in which the complex \( \text{NO}^+\text{H}_2\text{S} \) is solvated by a water molecule. The conversion from local to global minimum is associated with the transition state, \([\text{NO}^+\text{H}_4\text{SO}]^+\) (Fig. 3).

---

**Fig. 11**
Intermediate \( \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \cdot \text{HSNO} \)

**Fig. 12**
Reaction profiles for the cluster \( (\text{H}_2\text{O})_2 \cdot \text{NO}^+ \cdot \text{H}_2\text{S} \) (M1): ◆ \( \Delta E \) MP2, ■ \( \Delta E \) CCSD(T), ▲ \( \Delta H_{298} \), ■ \( \Delta G_{298} \)

The trajectory from the transition state to both minima was checked by the IRC procedure at the MP2/cc-pVTZ level. Although the agreement between BLYP, B3LYP and MP2 geometries is only qualitative, all three methods provide comparable structures associated with the isomerization path between local and global minimum. All attempts to locate the other stationary points eventually leading to proton transfer from H₂S to H₂O in this complex failed. This is in accord with previous studies which did not indicate proton transfer for any monosolvated species NO⁺X₂³.

We may consider five processes associated with the NO⁺H₂S·H₂O complex:

\[
\begin{align*}
\text{NO}^+\text{H}_2\text{S} + \text{H}_2\text{O} & \rightarrow \text{NO}^+\text{H}_2\text{S}\text{H}_2\text{O} \quad \text{(G)} \quad (1) \\
\text{NO}^+\text{H}_2\text{O} + \text{H}_2\text{S} & \rightarrow \text{NO}^+\text{H}_2\text{O}\cdot\text{H}_2\text{S} \quad \text{(L)} \quad (2) \\
\text{NO}^+\text{H}_2\text{S}\text{H}_2\text{O} & \rightarrow \text{NO}^+\text{H}_2\text{O}\cdot\text{H}_2\text{S} \quad (3) \\
\text{NO}^+\text{H}_2\text{S}\text{H}_2\text{O} & \rightarrow [\text{NO}^+\text{H}_4\text{SO}]^+ \quad \text{(TS)} \quad (4)
\end{align*}
\]

The first two refer to the formation of three-body complexes, the process (1) leads to the global minimum (denoted as G) while the process (2) leads to the local one (denoted as L). Conversion from the global to the local minimum can be accomplished via the transition state (TS, processes (3) and (4)). Energy quantities associated with the processes (1)–(4) are in Table I. The BSSE for (1) and (2) are small and amount to 3 and 6 kJ mol⁻¹, respectively. There is a significant entropy contribution in the association reactions (1) and (2) resulting in significantly lower complexation Gibbs energies than enthalpies, especially for the local minima (see also Figs 4 and 5). For the association reactions (1) and (2) both BLYP and B3LYP overestimate the enthalpy and Gibbs energy, compared with MP2 and CCSD(T) results. This means that not only electronic energies are overestimated by both DFT approaches but also the respective quantities entering the partition functions (frequencies, equilibrium geometries) differ significantly from MP2 data. This is clearly visible in Figs 4 and 5, energy profiles for MP2 and CCSD(T) are shallow compared with DFT approaches. The agreement between DFT approaches and MP2 or CCSD(T) is better for isomerizations ((3) and (4)), where favourable cancellation of errors takes place. Thus, for the future studies of dynamics and/or isomerizations in similar or
larger clusters, one can expect plausible results also from the BLYP or B3LYP levels of theory. Both temperatures (298 and 250 K) refer to the peak thermochemistry values between day and night. Hence, our results indicate that the potential accumulation of these complexes in the atmosphere most probably takes place during the night.

\[(\text{H}_2\text{O})_2\cdot\text{NO}^+\cdot\text{H}_2\text{S}\]

Attaching an additional water molecule to the global minimum G leads to a four-body cluster and has a dramatic effect on its chemistry, compared with the three-body cluster. The energy gain accompanying the association of the second water molecule (processes (5) and (10)) is only slightly smaller than pertinent \(\Delta H\) or \(\Delta G\) for the three-body cluster, reflecting strong coop-

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Energy profile (in kJ mol(^{-1})) for the (\text{NO}^+\cdot\text{H}_2\text{S}\cdot\text{H}_2\text{O}) complex</th>
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</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>Energy</td>
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<td>BLYP</td>
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</tr>
<tr>
<td>BLYP</td>
<td>(\Delta G_{298})</td>
</tr>
<tr>
<td>BLYP</td>
<td>(\Delta H_{250})</td>
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<tr>
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<td>B3LYP</td>
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<td>(\Delta H_{298})</td>
</tr>
<tr>
<td>MP2</td>
<td>(\Delta G_{298})</td>
</tr>
<tr>
<td>MP2</td>
<td>(\Delta H_{250})</td>
</tr>
<tr>
<td>MP2</td>
<td>(\Delta G_{250})</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>(\Delta H_{298})</td>
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<td>(\Delta H_{250})</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>(\Delta G_{250})</td>
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</tbody>
</table>

\(^a\) \(\Delta E_{\text{CCSD(T)}} = -68.0\) kJ mol\(^{-1}\), \(\Delta E_{\text{CCSD(T)}+\text{CPC}} = -61.6\) kJ mol\(^{-1}\). \(^b\) \(\Delta E_{\text{CCSD(T)}} = -41.6\) kJ mol\(^{-1}\), \(\Delta E_{\text{CCSD(T)}+\text{CPC}} = -38.6\) kJ mol\(^{-1}\).
eration effects in the formation of the four-body cluster. The BSSE for (5) is small (3 kJ mol$^{-1}$), we could not evaluate BSSE for process (10) because its calculation is obscured by a large geometry deformation in the resulting cluster (compared with subsystems) and thus not well defined. The three minima found on this potential energy surface are in Figs 6–8. Two of them (Figs 6 and 7) are complexes containing hydrogen bonded-network $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ in which the additional water molecule acts as a proton acceptor. The first complex, $(\text{H}_2\text{O})_2\cdot \text{NO}^+\cdot \text{H}_2\text{S}$ (denoted M1), is associated with the crossing of the transition state (Fig. 9) and its transformation to the intermediate $\text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\cdot \text{HSNO}$ (Fig. 11) and leading to hydrated hydroxonium cation and thionitrous acid:

$$\text{H}_2\text{O} + \text{H}_2\text{O} \cdot \text{NO}^+\cdot \text{H}_2\text{S} \rightarrow (\text{H}_2\text{O})_2 \cdot \text{NO}^+\cdot \text{H}_2\text{S} \quad \text{(M1)}$$

$$\hspace{1cm} (\text{H}_2\text{O})_2 \cdot \text{NO}^+\cdot \text{H}_2\text{S} \rightarrow \text{TS1} \quad \text{(6)}$$

$$\hspace{1cm} \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\cdot \text{HSNO} \rightarrow \text{TS1} \quad \text{(7)}$$

$$\hspace{1cm} (\text{H}_2\text{O})_2 \cdot \text{NO}^+\cdot \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\cdot \text{HSNO} \quad \text{(8)}$$

$$\hspace{1cm} \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\cdot \text{HSNO} \rightarrow \text{H}_3\text{O}^+ + \text{HSNO} \quad \text{(9)}$$

The second complex (M2, Fig. 7) is only slightly higher in energy than M1, the differences in $\Delta H$ or $\Delta G$ (see columns 2 in Tables II and III) not exceeding 4 kJ mol$^{-1}$. Both electronic states (M1 and M2) are probably nearly degenerate. The complex M2 is associated with the analogous series of reactions:

$$\text{H}_2\text{O} + \text{H}_2\text{O} \cdot \text{NO}^+\cdot \text{H}_2\text{S} \rightarrow (\text{H}_2\text{O})_2 \cdot \text{NO}^+\cdot \text{H}_2\text{S} \quad \text{(M2)}$$

$$\hspace{1cm} (\text{H}_2\text{O})_2 \cdot \text{NO}^+\cdot \text{H}_2\text{S} \rightarrow \text{TS2} \quad \text{(11)}$$

$$\hspace{1cm} \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\cdot \text{HSNO} \rightarrow \text{TS2} \quad \text{(12)}$$

$$\hspace{1cm} (\text{H}_2\text{O})_2 \cdot \text{NO}^+\cdot \text{H}_2\text{S} \rightarrow \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+\cdot \text{HSNO} \quad \text{(13)}$$

The bent hydrogen bond \( \text{H}_2\text{O} \cdots \text{HOH} \) present in both minima is the crucial point in the transformation of the \( (\text{H}_2\text{O})_2 \cdot \text{NO}^+ \cdot \text{H}_2\text{S} \) isomers because this hydrogen bond is the driving force for the rearrangement of the protons in the \( \text{H}_2\text{O} \cdots \text{H}_2\text{O} \cdots \text{H}_2\text{S} \) thread. The water molecule in the centre of the cluster promotes further proton transfer from \( \text{H}_2\text{S} \) to the water dimer (processes of forming TS1 or TS2). The elongation of the pertinent HS-bond from equilibrium position \( \sim 1.36/1.37 \ \text{Å} \) (M1/M2, Figs 6 and 7) to \( \sim 1.47/1.49 \ \text{Å} \) (TS1/TS2).

**TABLE II**

Energy profile (in kJ mol\(^{-1}\)) for the complex \( (\text{H}_2\text{O})_2 \cdot \text{NO}^+ \cdot \text{H}_2\text{S} \) (M1). Thermodynamic quantities are based on CCSD(T) energies

<table>
<thead>
<tr>
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<th>(9)</th>
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</tr>
</tbody>
</table>

\(^a\) \( \Delta E_{\text{CCSD(T)}+\text{CPC}} = -55.7 \ \text{kJ mol}^{-1} \) for process (5).

**TABLE III**

Energy profile (in kJ mol\(^{-1}\)) for the complex \( (\text{H}_2\text{O})_2 \cdot \text{NO}^+ \cdot \text{H}_2\text{S} \) (M2). Thermodynamic quantities are based on CCSD(T) energies

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</tbody>
</table>

Figs 9 and 10) can be followed. The activation processes (6) and (11) (Tables II and III) are accompanied by negligible energy changes (the $\Delta H$ or $\Delta G$ estimates are even negative) but this is the effect of ZPV and thermal corrections. Energy profiles in Fig. 12 offer an alternative picture of the conversion of the cluster from the minimum structure M1 into hydrated intermediate $\text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \cdot \text{HSNO}$. The negative CCSD(T) barrier is most probably a geometry effect, since this is a result of single-point calculation at the MP2 geometry. The reverse processes (7) and (12) are associated with larger barriers indicating slower recombination rates once the intermediate $\text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \cdot \text{HSNO}$ has been formed. Again, one can observe large entropy effect. Thus, the structures M1 and M2 are reactive species which are the potential source of hydrated HSNO in the atmosphere.

The third complex (M3, Fig. 8) can be regarded as an association product of the global minimum of the three-body cluster with a second water molecule. Our calculations indicate that its formation is accompanied by similar energy changes as the formation of M1 and M2, e.g., $\Delta H_{298} = -52.6 \text{ kJ mol}^{-1}$ and $\Delta G_{298} = -23.6 \text{ kJ mol}^{-1}$ (based on CCSD(T) energies). This cluster represents a quasi-symmetrical structure that is not reactive, i.e., it does not provide any mechanism for the rearrangement of protons because of the unfavourable $\text{H}_2\text{O} \cdots \text{H}_2\text{S} \cdots \text{H}_2\text{O}$ network (see Fig. 8) which represents merely electrostatic coordination of the ligands around the $\text{NO}^+$ cation. However, further hydration of this cluster may lead to a similar hydrogen-bonded network and promotion of proton transfer leading to thionitrous acid. Work is in progress along these lines in our laboratory.

**CONCLUSIONS**

We have shown that nitrosonium cation can form stable but relatively weakly-bound complexes with hydrogen sulfide and water under both laboratory and atmospheric conditions. The binding energy is of the order of a medium-strength hydrogen bond. Gradual addition of water molecules changes dramatically the chemistry of clusters. The calculations indicate that the three-body clusters, $\text{NO}^+ \cdot \text{H}_2\text{S} \cdot \text{H}_2\text{O}$ or $\text{NO}^+ \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{S}$ once formed, do not undergo further changes and may serve merely as a reservoir for subsequent formation of higher clusters. On the other hand, the four-body cluster, possessing a favorable hydrogen bond, may easily be converted to the thionitrous acid. Our model calculations indicate that the transformation of the four-body cluster depends on the approach of a second water molecule. Therefore, for better understanding of $\text{NO}^+$ clustering and related chemistry, it is desirable to study also the dynamics of these clusters scan-
ning a larger number of possible trajectories at temperatures mimicking the conditions of the upper atmosphere.

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