Protonation of $N_2O$ and $NO_2$ in a solid phase†

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Adsorption of gaseous $N_2O$ on the acidic surface Brønsted centers of the strongest known solid acid, $H(CHB_{11}F_{11})$, results in formation of the $N≡N−OH^+$ cation. Its positive charge is localized mainly to the H-atom, which is H-bonded to the $CHB_{11}F_{11}^-$ anion forming an asymmetric proton disolvate of the $L_1−H^+−L_2$ type, where $L_1 = N_2O$ and $L_2 = CHB_{11}F_{11}^-$. $NO_2$ protonation under the same conditions leads to the formation of the highly reactive cation radical $NO_2H^+$, which reacts rapidly with an $NO_2$ molecule according to the equation $N_2OH^+ + NO_2 → [N_2O_2H^+] → N_2OH^+ + O_2$ resulting in the formation of two types of $N_2OH^+$ cations: (i) a typical Brønsted superacid, $N≡N−OH^+$, with a strongly acidic OH group involved in a rather strong H-bond with the anion, and (ii) a typical strong Lewis acid, $N≡N−OH$, with a positive charge localized to the central N atom and ionic interactions with the surrounding anions via the charged central N atom.

Introduction

Weakly basic small molecules $H_2$, $N_2$, $O_2$, $CO_2$, $CO$, $N_2O$, $NO_2$ are interesting targets for protonation. No evidence has been obtained for the protonation of these simple gaseous molecules under ambient conditions in a “magic” superacid system, $HSO_3F−SbF_5−SO_3$, one of the strongest known mixed Brønsted/Lewis acids. Nonetheless, a somewhat stronger HF/SbF$_5$ mixed acid system can protonate CO, when it is dissolved, but under conditions of high pressure (up to 85 atm). The corresponding salt is not isolable. Using a newly synthesized strongest solid superacid, $H(CHB_{11}F_{11})$, we have been able to protonate CO under ambient conditions both through the C atom and via the O atom and to obtain in preparative quantities bulk salts of the $H^+CO$ and $CO^+H$ cations. Therefore, the $H(CHB_{11}F_{11})$ acid manifests itself as stronger than the “magic” acids, and is expected to protonate (under ambient conditions) other, less basic than CO, molecules such as $N_2O$ and $NO_2$, which still cannot be protonated in a condensed phase. In a gas phase, the protonation of small molecules was proved by mass spectroscopy and IR spectroscopy. For example, $N_2O$ is protonated via the O atom, and the frequency of the O−H$^+$ stretch was found to be 3331 cm$^{-1}$ for the gas phase, and 43.3 cm$^{-1}$ lower for the Ne matrix. The experimental difficulties with the protonation of the simple molecules are compensated so far by the research in this field on the basis of quantum-chemical calculations, that confirmed that the O-protonated isomer ($NNOH^+$) is energetically more preferable (by 4.02 kcal mol$^{-1}$) than the N-protonated isomer.

Recently, it was reported that $CO_2$ is protonated by $H(CHB_{11}F_{11})$ with the formation of a stable (at room temperature) salt of the symmetric disolvate $OCO−H^+−OCO$. This seems unexpected because $CO_2$ being more basic than $CO$, forms under the same conditions only salts of the $L_1−H^+−L_2$ type cations with an asymmetric bridged proton, where $L_1 = CO$ and $L_2 = CHB_{11}F_{11}^−$ anion. The basicity of $CO$ is not sufficient to substitute $L_1$ for the formation of symmetric OC$−H^+−CO$. It is interesting to test whether other weakly basic molecules, $N_2O$ or $NO_2$, can form the symmetric disolvates L$−H^+−L$. Moreover, the carboxide salts of the protonated nitrogen oxides must have superacidic properties, as salts of the COH$^+$ cation, and can serve as the reagents for obtaining new types of functionalized carbocations.

In the present work, we studied the protonation of $N_2O$ and $NO_2$ by the strongest known solid carborane superacid, $H(CHB_{11}F_{11})$ (Fig. 1), using the methods of infrared (IR) spectroscopy and quantum chemistry.

![Fig. 1 Icosahedral carborane anions, CHB_{11}F_{11}^−, with the numbering of three types of F atoms differing in basicity.](image)
Experimental

Carborane acid H(CHB$_1$F$_{11}$) hereafter abbreviated as H(F$_{11}$) was prepared as previously described.$^3$ IR spectroscopic analysis of the interaction of N$_2$O or NO$_2$ with H(F$_{11}$) was performed as follows. The solid acid was sublimed at 150–160 °C under a pressure of 10$^{-5}$ Torr on cold Si windows in a specially designed IR cell reactor, forming a very thin translucent film of the amorphous acid.$^5$ Dry gaseous N$_2$O or NO$_2$ (obtained from Sigma Aldrich, 99% purity), was injected anaerobically into the IR cell inside a dry box and reacted with the acid at room temperature. IR spectra were recorded at certain time intervals. Weigable amounts of the N$_2$OH$^+$ [F$_{11}$]$^-$ salt were obtained by aging of a portion of H(F$_{11}$) for 1 day in a Schlenk tube filled with N$_2$O.

All procedures were performed in a Spectro-systems glove-box under an atmosphere of Ar (H$_2$O < 1 ppm). The IR spectra were recorded on an Bruker Vector 22 spectrometer inside a dry box in either transmission or attenuated total reflectance (ATR) mode (525–4000 cm$^{-1}$). The IR data were processed with the GRAMMS/A1 (7.00) software from Thermo Fisher Scientific.

Computational details

The geometric parameters of the species under study were optimized at the B3LYP-D3/def2-TZVPD level of theory$^{26-29}$ with an ultrafine grid. The equilibrium structures of the specific compounds were also calculated in a dichloroethane (DCE) box in either transmission or attenuated total reflectance (ATR) mode. The IR data were processed with the GRAMMS/A1 (7.00) software from Thermo Fisher Scientific.

Results of calculations

The gas phase B3LYP-D3/def2-TZVPD calculations of [F$_{11}$]$^-$ containing compounds do not fully describe the ionic interactions taking place in the solid state, leading to a bad agreement between some calculated and experimental vibrational frequency values of the cations (Fig. S1–S3, ESI†). For this reason, we performed calculations for the N$_2$OH$^+$...L and NO$_2$H$^+$...L model systems, where L = Ar, Kr, Xe, CO, or SO$_2$. A wide range of L basicities, which includes the basicity of the [F$_{11}$]$^-$ anion, allows us to interpret the experimental IR spectra more correctly (Fig. S4, ESI†). To model the effect of the environment playing an important role in crystals, we also conducted SMD-B3LYP-D3/def2-TZVPD calculations in a DCE solution for the compounds of interest (Fig. S5, ESI†).

(N$_2$O)$^+$ cation

Protonation of N$_2$O is possible via terminal N and O atoms (Fig. S1, ESI†). The O-protonated structure is more stable (the energy difference between the O–H$^+$ and N–H$^+$ isomers is 3.9 kcal mol$^{-1}$ at the CCSD[T]/def2-TZVPD/B3LYP-D3/def2-TZVPD level of theory; Fig. S1, ESI†), which is in line with other experimental$^{12}$ and theoretical studies.$^{17-19,22-24}$

N$_2$O described by the N-oxide valence formula, N≡N$^-$O$^+$ (Fig. S6, ESI†), has two valence frequencies (Table S1, ESI†), $\nu_{N_2}$N$_2$O at 2268 cm$^{-1}$ and $\nu_{N_2}$N$_2$O at 1285 cm$^{-1}$, which can be represented as the characteristic vibrations of the NN and NO stretches, respectively. The bent vibration is at 598 cm$^{-1}$.

Protonation of N$_2$O leads to formation of the N≡N–OH$^+$ cation (Fig. S7a, ESI†), with a significant decrease in the NO stretch (∼250 cm$^{-1}$) and an increase in the NN stretch (by ∼90 cm$^{-1}$; Table S2, ESI†) because the N–O and N≡N bonds approach the common single and triple bond respectively.

According to vibrational analysis, the solvation of N$_2$OH$^+$ by Ar, Kr, or Xe weakened the OH bond and strengthened the NO bond (Table S2, ESI†). The dependence of the $\nu$NO frequency (reflecting the N–O strength) on the proton affinity (PA) of the noble gases (L) is linear (Fig. 2) confirming that the N–O stretch is highly characteristic because the (N$_2$O)H$^+$–L bond is ionic. Nevertheless, the analogous dependences for $\nu$OH and $\nu$NN frequencies deviate from the linear function to a greater extent with the greater basicity of L because a decrease in the frequency of OH$^+$ stretch and an increase in the frequency of the NN stretch result in their convergence with an enhancement of their interaction. This mixing becomes more notable when N$_2$OH$^+$ is solvated by the stronger bases, CO, SO$_2$, and [F$_{11}$]$^-$, which formed a partially covalent bond with a cation.

This situation leads to the formation of a rather asymmetric proton disolvate of the L$_1$–H$^+$...L$_2$ type (L$_1$ = N$_2$O; L$_2$ = SO$_2$,
\(\text{(NO}_2\text{)}\text{H}^+\) cation

The \(\text{NO}_2\) molecule has two stretch vibrations, \(\nu_{\text{asNO}_2}\) and \(\nu_s\text{NO}_2\), with a frequency difference \(\Delta = 295 \text{ cm}^{-1}\) (Table S1, ESI†). After protonation, the radical cation \(\text{NO}_2\text{H}^+\) is formed (I.B.1 structure; Fig. S2, ESI†) having \(\text{NO}\) and \(\text{NO(H)}\) stretches with increased and decreased frequencies, respectively, as compared to \(\text{NO}_2\) (Table S3, ESI†). Their difference \(\Delta\) increased to 727 \text{ cm}^{-1} indicating that the stretching vibrations acquire some characteristic nature. The solvation of \(\text{(NO}_2\text{)}\text{H}^+\) with \(\text{Ar}\) decreases both \(\text{NO}\) stretches keeping their difference \(\Delta\) actually unchanged. When the cation is solvated with stronger bases, \(\text{Kr}\) and \(\text{Xe}\), the \(\text{O-H}^+\) bond continues to weaken (\(\nu\text{OH}^+\) decreases), thus strengthening the \(\text{N-O(H)}^+\) bond and its frequency (Table S3, ESI†). With a further increase in the basicity of \(\text{L} (\text{CO, SO}_2)\), \(\text{H}^+\) of \(\text{(NO}_2\text{)}\text{-H}^+\cdot\cdot\cdot\text{L}\) became a typical bridged proton with stretch frequencies of 1500–1100 \text{ cm}^{-1}.

(N\(_2\text{O}_4\))\text{H}^+ cation

Gaseous \(\text{NO}_2\) is always in equilibrium with \(\text{N}_2\text{O}_4\). Accordingly, the protonation of \(\text{NO}_2\) may be accompanied by the protonation of \(\text{N}_2\text{O}_4\). The latter is unstable, which is related to the large \(\text{N-N}\) bond length of 1.78 Å. After protonation, the optimized structure of \(\text{N}_2\text{O}_4\text{H}^+\) (Ic10 in Fig. S4, ESI†) showed a significant increase in the \(\text{N-N}\) distance (2.247 Å), which precluded its formation. Solvation of the \(\text{N}_2\text{O}_4\text{H}^+\) cation with such bases as \(\text{Ar, CO, SO}_2, \) or \(\{\text{F}_{11}\}\), reduced the \(\text{N-N}\) distance down to 2.179, 2.079, 2.023, and 1.909 Å respectively, but it was still big enough for the cation to exist. Calculations predicted that unstable \(\text{N}_2\text{O}_4\text{H}^+\cdot\cdot\cdot\text{L}\) can decompose in the simplest way into a \(\text{(HNO}_3\text{)}\cdot\cdot\cdot\text{L}\) compound (Fig. S4, S5 and Tables S4, S5, ESI†). In any case, it is expected that the protonation of \(\text{N}_2\text{O}_4\) will lead to subsequent secondary reactions.

**Experimental results**

**\(\text{N}_2\text{O}\) interaction with the \(\text{H(}\text{F}_{11}\text{)}\) acid**

After injection of \(\text{N}_2\text{O}\) into the IR cell-reactor with the sublimed \(\text{H(}\text{F}_{11}\text{)}\) acid, we started to register the IR spectra immediately. Subtraction from these spectra of the spectrum of gaseous \(\text{N}_2\text{O}\) revealed a weak band at \(2231 \text{ cm}^{-1}\), which is very close to the \(\nu\text{NN}\) band at \(2224 \text{ cm}^{-1}\) of gaseous \(\text{N}_2\text{O}\), but without the fine vibrational structure (Fig. 3). Obviously, this pattern denotes \(\text{N}_2\text{O}\) molecules absorbed by the acidic surface Brønsted centers of solid \(\text{H(}\text{F}_{11}\text{)}\). After vacuum removal of the gaseous \(\text{N}_2\text{O}\), the band at \(2311 \text{ cm}^{-1}\) persisted, but after fast heating up to 100 °C in a sealed vacuumed cell, this band disappeared and a weak spectrum of gaseous \(\text{N}_2\text{O}\) appeared. Therefore, \(\text{N}_2\text{O}\) molecules are indeed adsorbed to the surface Brønsted centers of the \(\text{H(}\text{F}_{11}\text{)}\) acid, and this sorption is relatively strong.

With time, in the IR spectra, two narrow bands of NN stretches of \(\text{N}_2\text{OH}^+\) cations appeared and grew in intensity: at 2363 \text{ cm}^{-1} and at 2320 \text{ cm}^{-1} (Fig. 3). They belong to cations...
that bind to the most basic “b” and “c” sites of the \( \{F_{11}^-\} \) anion (hereinafter referred to as \( \text{N}_2\text{OH}_b \) and \( \text{N}_2\text{OH}_c \)), as is the case for \( \text{H}^+ \text{CO} \) binding to \( \{F_{11}^-\} \). Simultaneously, the absorption corresponding to the free (unreacted) \( \text{H}\{F_{11}\} \) acid decreases and after 8–10 h disappears (judging by the indicative band at 1616 cm\(^{-1}\) of the stretch vibration of the bridged proton in polymeric acid [\( \text{H}\{F_{11}\}_\text{poly} \), Fig. 3]. In the low-frequency region of the \( \text{N}^-\text{O}(\text{H}^+) \) stretches, weak complex bands appeared at 1068 and 1073 cm\(^{-1}\), which correspond to \( \text{N}_2\text{OH}^-_c \) and \( \text{N}_2\text{OH}^+_b \), respectively (Fig. 5).

Fig. 4 shows the intensity dependences of the bands of the NN stretches from \( \text{N}_2\text{OH}_b \) and \( \text{N}_2\text{OH}_c \) (\( A_{\text{NN}} \) at 2321 or 2364 cm\(^{-1}\) respectively) on the absorption intensity of the acid being used (an intensity decrease at 1616 cm\(^{-1}\), \( A_{1616} \)). The figure shows that the formation of the \( \text{N}_2\text{OH}^-_b \) and \( \text{N}_2\text{OH}^+_c \) cations initially increased proportionally. Then, the filling of the most basic “c” site of \( \{F_{11}^-\} \) reached saturation, while the filling of the “b” site continued.

The absorption corresponding to the O–H+ stretch is expected to be very broad and cannot be detected with certainty. To detect it, we used the following method. After completion of the reaction, gaseous \( \text{N}_2\text{O} \) was removed by evacuation. The cell was sealed and heated to 100°C for 5 min. The IR spectrum shows the emergence of a weak band of the bridged proton of the free \( \text{H}\{F_{11}\} \) acid at 1616 cm\(^{-1}\). The character of changes in the intensity of this band is that of 2223 cm\(^{-1}\) (Fig. 6) which, without a doubt, belongs to the bridged proton of the free \( \text{H}\{F_{11}\} \) acid at 1616 cm\(^{-1}\) appeared as well. That is, reaction (1) of \( \text{N}_2\text{OH}^+ \) decomposition takes place.

\[
\text{N}_2\text{OH}^+ \{F_{11}^-\} \xrightarrow{100^\circ C} \text{N}_2\text{O} + \text{H}\{F_{11}\} \quad (1)
\]

Partial decomposition of \( \text{N}_2\text{OH}^+ \) should decrease the absorption corresponding to the O–H+ stretch. This allows us, by calculating the difference in the spectra before and after heating, to detect the absorption corresponding to the O–H+ stretch with positive intensity, whereas the absorption corresponding to the H-vibrations of \( \text{H}\{F_{11}\} \) will have negative intensity.

As shown in Fig. 5 and Fig. S10 (in ESI†), \( \nu(\text{O–H}^+) \) emerges as a broad band at \( ca. 2000 \) cm\(^{-1}\).

### Interaction of \( \text{NO}_2 \) with the \( \text{H}\{F_{11}\} \) acid

Interaction of gaseous \( \text{NO}_2 \) with a thin film of the amorphous polymeric acid on the Si windows of the IR cell reactor results in a decreasing absorption band of the bridged proton of the \( \text{H}\{F_{11}\} \) acid at 1616 cm\(^{-1}\) and the appearance of new bands of the formed compounds (Fig. 6). The reaction finished after \( ca. 3 \) h.

IR spectra of the resulting products do not contain bands of the \( \text{NO}_2\text{H}^+ \cdots \cdot \text{L} \) type compounds predicted by calculations (Table S3, ESI†) but show bands of the stretch vibrations in the frequency region of 2300–2400 cm\(^{-1}\) belonging to the other compounds. One of these bands at 2364 cm\(^{-1}\) coincides exactly with that of \( \text{N}_2\text{OH}^+_c \). Moreover, as the reaction of \( \text{NO}_2 \) with \( \text{H}\{F_{11}\} \) proceeded, the band of the NN stretch at 2223 cm\(^{-1}\) of gaseous \( \text{N}_2\text{O} \) emerged and increased in intensity (Fig. 6, inset). The dependence of the intensity of the band at 2364 cm\(^{-1}\) on that of 2223 cm\(^{-1}\) is strictly proportional (Fig. 7); this result confirmed the joint formation of \( \text{N}_2\text{OH}^+_c \) and \( \text{N}_2\text{O} \) in the course of the secondary reactions that take place between the initially formed \( \text{NO}_2\text{H}^+_c \) and gaseous \( \text{NO}_2 \).

A distinctive band of the second compound at 2334 cm\(^{-1}\) is typical in terms of frequency for the NN stretch of the \( \text{N}_2\text{OH}^+ \) cation but did not coincide with that of \( \text{N}_2\text{OH}_b \) discussed above. The character of changes in the intensity of this band is manifested in a certain relation with another band in the spectra at 3560 cm\(^{-1}\) (Fig. 6) which, without a doubt, belongs to OH stretch vibrations (IR spectra did not show the bands from the OH stretches of the \( \text{H}_2\text{O}^+ \) cation). The dependence of the intensity of the band at 2334 cm\(^{-1}\) on that of \( \nu\text{OH} \) at 3560 cm\(^{-1}\) is directly proportional (Fig. 8), which means that they belong to one compound. A sample of this compound was obtained when a powder of the \( \text{H}\{F_{11}\} \) acid (precipitated in liquid HCl during its synthesis) was aged in an atmosphere of \( \text{NO}_2 \). At a low partial pressure of \( \text{NO}_2 \) (\( ca. 0.2 \) atm) presumably \( \text{N}_2\text{OH}_b^+ \) is formed, whereas at a higher partial pressure (\( ca. 0.8 \) atm) the second compound mainly is formed (Fig. 9a). The only new band detected in the spectrum of the second compound
is at 1045 cm\(^{-1}\), which is common for the N–O(H) stretch frequency (Fig. 9b and Table S2, ESI†). The sample was placed on the bottom of the IR cell reactor, and after addition of a drop of water, the cell was sealed. The IR spectra registered the appearance of the absorption pattern of gaseous N\(_2\)O. Thus, the second compound is the salt of the N\(_2\)OH\(^+\) cation with a free OH bond (further denoted as N\(_2\)OH\(_{\text{free}}\)\(^+\)), which is decomposed by water with N\(_2\)O elimination.

Finally, the third band in the frequency range of the NN stretch appears at 2307 cm\(^{-1}\) after long aging of the sample under an atmosphere of NO\(_2\) (more than 24 h, Fig. 6). We propose that it emerges due to water vapor penetration. We verified this idea by introducing water vapor into the IR cell along with the N\(_2\)OH\(^+\)\(_{\text{F11}}\) salt and observed rapid disappearance of the bands of the NN stretches of the N\(_2\)OH\(^+\) and N\(_2\)OH\(_{\text{free}}\)\(^+\) cations, but the band at 2307 cm\(^{-1}\) persisted and even increased in intensity (Fig. S11 in ESI†). This finding indirectly confirms the affiliation of this band with the hydrated species.
Discussion

Comparison of the empirical spectra of N₁OH−ₐ and N₂OH−ₐ cations (Table 1) with the calculated spectra (Table S2, ESIT) shows that these cations belong to the L₁−H−⋯L₂ type, where L₁ = N₂O and L₂ = {F₁₁−} anion with “b” and “c” basic sites. These empirical spectra show the greatest congruence with those calculated for the N₃OH−⋯Kr and N₄OH−⋯Xe solvates (Table S2, ESIT); in particular, the νN−O frequency almost coincides with that of N₃OH−⋯Kr (Fig. 2). This result implies that an “effective” PA of {F₁₁−} in the solid N₂OH−{F₁₁−} salt is close to that of the Kr atom. Moreover, the positive charge and electron density redistribution over the N− atom, as well as the geometric parameters of these groups, determined by means of calculations, should be very close to those of N₂OH−ₐ and N₄OH−ₐ. Thus, these cations can be described as having the NNO angle close to 180° with the triple N≡N (ca. 1.001 Å) and single N−O(H⁺) bonds (ca. 1.252 Å) in accordance with the N oxide valence formula N≡N−OH. On the other hand, the O−H stretch at ca. 2000 cm⁻¹ indicates strong H-bonding with the {F₁₁−} anion having the positive charge mainly on the H (Scheme 1).

Attempts to protonate NO₂ led to an unexpected result: the spectrum of the cation radical NO₂H⁺ predicted by calculations (Table S3, ESIT) is not registered, but the spectrum of N₂OH⁺ cations appeared. Obviously, there is a rapid transition from NO₂H⁺ to the N₂OH⁺ cation, which can only take place via reaction (2)

\[
\text{NO}_2\text{H}^+ + \text{NO}_2 \rightarrow \text{N}_2\text{O}^+ + \text{O}_2 \tag{2}
\]

because the formation of other nitrogen oxides was not registered by IR spectroscopy either in the solid phase or in the gas phase. Unfortunately, O₂ generated by reaction (2) is not detected by IR spectroscopy. Eqn (2) is suggestive of the formation of an intermediate: the protonated dimer of nitrogen dioxide, N₂O₂H⁺. This cation can also be formed by the direct protonation of N₂O₂, which is present in amounts comparable with those of NO₂ in the gaseous mixture. Unstable N₂O₂H⁺ further decomposes into N₂OH⁺ in accordance with eqn (3)

\[
\text{N}_2\text{O}_2\text{H}^+ \rightarrow \text{N}_2\text{O}^+ + \text{O}_2 \tag{3}
\]

It was a surprise that one of the two N₂OH⁺ cations formed in reactions (2) or (3) is N₂O₂H⁻ with a free OH group, which is not H-bonded to the {F₁₁−} anion. This means that N₂O₂H⁻, exactly matches the N oxide valence formula N≡N−OH with the positive charge located on the central N atom. The stretch O−H frequency of N₂O₂H⁻ is higher (3560 cm⁻¹) than that of the free cation in vacuum, both calculated (3332 cm⁻¹) and empirically determined (3331 cm⁻¹). This means that the interaction of N₂O₂H⁻ with the neighboring {F₁₁−} anions is purely ionic and proceeds via the N atom (Scheme 2) leading to polarization of the OH group and an increase in its stretch frequency so much that it even exceeds the value corresponding to naked N₂OH⁻ in vacuum. Thus, N₂O₂H⁻ is an unusual representative of a pure Lewis acid with a covalent OH group.

Cation radical NO₂H⁺, formed in the first step of NO₂ protonation with H{F₁₁}, according to calculations (Table S5, ESIT), is stable. Nevertheless, as experiments showed, it has high reactivity and quickly reacts with the next NO₂ molecule (eqn (2)) forming an unstable intermediate, N₂O₄H⁺. According to calculations, the instability of N₂O₄H⁺ is caused by extension of the N−N bond up to 2.247 Å. The simplest route of its decomposition is formation of the HNO₂−NO⁺ solvate (Fig. S4, S5 and Table S5 in ESIT). In contrast, the experiment shows that decomposition of N₂O₄H proceeds via eqn (3) to N₂OH⁺ + O₂.

The fact that there is a proportionality between the amount of the formed N₂OH⁺ and gaseous N₂O (Fig. 2) indicates the existence of an equilibrium N₂O₄H⁺ {F₁₁−} = N₂O + H{F₁₁}, which, however, is absent between N₂O₄H⁻ and gaseous N₂O. That is, N₂O₂H⁻ is formed only through N₂O₂H⁺ decomposition.

Conclusion

Gaseous N₂O and NO₂ are protonated under ambient conditions with the strongest known solid superacid, H{F₁₁}. N₂O is attached...
to the H atom of the polymeric (H[F11])ₙ acid at the first stage via physical adsorption without breaking the bridge H-bond and proton transfer to the N₂O molecule (Scheme 3, left). The adsorbed N₂O molecules are not desorbed in vacuum at room temperature, but are easily detached at elevated temperatures.

The second stage is the breakage of the –[F₁₁]–H–[F₁₁]– hydrogen bridge and proton transfer to the O atom of N₂O (Scheme 3). The formed N₂OH⁻ cation retains a fairly strong H bond with the [F₁₁⁻] anion, attaching to its “b” or “c” site (Scheme 1). This compound can be regarded as an asymmetric proton solvate, L₁⁻H⁺···L₂, with L₁ = N₂O and L₂ = counterion.

Adsorption of NO₂ on the surface of the H[F₁₁] acid did not reveal the IR absorption pattern of physically adsorbed NO₂ or protonated NO₂ because the cation radical NO₂H⁺, which obviously must be formed, has high reactivity. It quickly interacts with NO₂ forming an unstable intermediate, N₂O₂H⁺, which decomposes (eqn (3)) forming two types of N₂OH⁺ cations. The first one is N₂OH⁺ with a common H-bonding to the [F₁₁⁻] ion. The second one, N₂OH⁺free, is unusual in that it has a free non-acid OH group with a positive charge localized to the central N atom, which enters into an ionic interaction with anions in the environment (Scheme 2). Thus, if the first N₂OH⁺ cation is a typical Brønsted superacid, then the second cation, N₂OH⁺free, is a strong Lewis acid that is formed only as a result of a chemical reaction, but not as a result of the sorption or desorption interaction.

The present work shows that N₂O, just as CO studied earlier, during protonation by the H[F₁₁] acid, cannot form a symmetric proton solvate of the L–H⁺–L type in the solid phase. For this reason, the results of another article [ref. 25]—claiming that CO₂, less basic than either N₂O or CO, forms the stable salt of the proton disolvate under ambient conditions—are questionable, especially because the supporting experimental evidence is not convincing.

Conflicts of interest
There are no conflicts to declare.

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