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## Protonation of N<sub>2</sub>O and NO<sub>2</sub> in a solid phase†

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Adsorption of gaseous N<sub>2</sub>O on the acidic surface Brønsted centers of the strongest known solid acid, H(CHB<sub>11</sub>F<sub>11</sub>), results in formation of the N≡N–OH<sup>+</sup> cation. Its positive charge is localized mainly to the H-atom, which is H-bonded to the CHB<sub>11</sub>F<sub>11</sub><sup>−</sup> anion forming an asymmetric proton disolvate of the L<sub>1</sub>–H<sup>+</sup>⋯L<sub>2</sub> type, where L<sub>1</sub> = N<sub>2</sub>O and L<sub>2</sub> = CHB<sub>11</sub>F<sub>11</sub><sup>−</sup>. NO<sub>2</sub> protonation under the same conditions leads to the formation of the highly reactive cation radical NO<sub>2</sub>H<sup>•+</sup>, which reacts rapidly with an NO<sub>2</sub> molecule according to the equation N<sub>2</sub>OH<sup>+</sup> + NO<sub>2</sub> → [N<sub>2</sub>O<sub>4</sub>H<sup>+</sup>] → N<sub>2</sub>OH<sup>+</sup> + O<sub>2</sub> resulting in the formation of two types of N<sub>2</sub>OH<sup>+</sup> cations: (i) a typical Brønsted superacid, N≡N–OH<sup>+</sup>, 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<sup>+</sup>–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<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>O, NO<sub>2</sub> 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<sub>3</sub>F–SbF<sub>5</sub>–SO<sub>3</sub>,<sup>1</sup> one of the strongest known mixed Brønsted/Lewis acids. Nonetheless, a somewhat stronger HF/SbF<sub>5</sub> mixed acid system can protonate CO, when it is dissolved, but under conditions of high pressure (up to 85 atm).<sup>2,3</sup> The corresponding salt is not isolable. Using a newly synthesized strongest solid superacid, H(CHB<sub>11</sub>F<sub>11</sub>),<sup>4</sup> 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<sup>+</sup>CO and COH<sup>+</sup> cations.<sup>3</sup> Therefore, the H(CHB<sub>11</sub>F<sub>11</sub>) 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<sub>2</sub>O and NO<sub>2</sub>, which still cannot be protonated in a condensed phase. In a gas phase, the protonation of small molecules was proved by mass spectroscopy<sup>5–10</sup> and IR spectroscopy.<sup>11–13</sup> For example, N<sub>2</sub>O is protonated *via* the O atom, and the frequency of the O–H<sup>+</sup> stretch was found to be 3331 cm<sup>−1</sup> for the gas phase,<sup>12,13</sup> and 43.3 cm<sup>−1</sup> lower for the Ne matrix.<sup>14</sup> 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,<sup>15–24</sup>

that confirmed that the O-protonated isomer (NNOH<sup>+</sup>) is energetically more preferable (by 4.02 kcal mol<sup>−1</sup>)<sup>24</sup> than the N-protonated isomer.

Recently, it was reported<sup>25</sup> that CO<sub>2</sub> is protonated by H(CHB<sub>11</sub>F<sub>11</sub>) with the formation of a stable (at room temperature) salt of the symmetric disolvate OCO–H<sup>+</sup>–OCO. This seems unexpected because CO, being more basic than CO<sub>2</sub>, forms under the same conditions only salts of the L<sub>1</sub>–H<sup>+</sup>⋯L<sub>2</sub> type cations with an asymmetric bridged proton, where L<sub>1</sub> = CO and L<sub>2</sub> = CHB<sub>11</sub>F<sub>11</sub><sup>−</sup> anion.<sup>3</sup> The basicity of CO is not sufficient to substitute L<sub>2</sub> for the formation of symmetric OC–H<sup>+</sup>–CO. It is interesting to test whether other weakly basic molecules, N<sub>2</sub>O or NO<sub>2</sub>, can form the symmetric disolvates L–H<sup>+</sup>–L. Moreover, the carborane salts of the protonated nitrogen oxides must have superacidic properties, as salts of the COH<sup>+</sup> cation,<sup>3</sup> and can serve as the reagents for obtaining new types of functionalized carbocations.

In the present work, we studied the protonation of N<sub>2</sub>O and NO<sub>2</sub> by the strongest known solid carborane superacid, H(CHB<sub>11</sub>F<sub>11</sub>) (Fig. 1), using the methods of infrared (IR) spectroscopy and quantum chemistry.

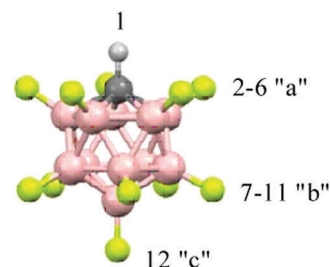


Fig. 1 Icosahedral carborane anions, CHB<sub>11</sub>F<sub>11</sub><sup>−</sup>, with the numbering of three types of F atoms differing in basicity.

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## Experimental

Carborane acid  $\text{H}(\text{CHB}_{11}\text{F}_{11})$  hereafter abbreviated as  $\text{H}\{\text{F}_{11}\}$  was prepared as previously described.<sup>4</sup> IR spectroscopic analysis of the interaction of  $\text{N}_2\text{O}$  or  $\text{NO}_2$  with  $\text{H}\{\text{F}_{11}\}$  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.<sup>3</sup> Dry gaseous  $\text{N}_2\text{O}$  or  $\text{NO}_2$  (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. Weighable amounts of the  $\text{N}_2\text{OH}^+\{\text{F}_{11}^-\}$  salt were obtained by aging of a portion of  $\text{H}\{\text{F}_{11}\}$  for 1 day in a Schlegel tube filled with  $\text{N}_2\text{O}$ .

All procedures were performed in a Spectro-systems glove-box under an atmosphere of Ar ( $\text{H}_2\text{O} < 1$  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  $\text{cm}^{-1}$ ). 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<sup>26–29</sup> with an ultrafine grid. The equilibrium structures of the specific compounds were also calculated in a dichloroethane (DCE) solution using the SMD solvation model.<sup>30</sup> All stationary points were characterized as minima by a vibrational analysis (the number of imaginary frequencies was equal to zero). Zero-point energies were computed from the corresponding vibrational frequencies without scaling factors. (SMD)-B3LYP-D3/def2-TZVPD optimized structures were used in all subsequent computations.

To compare the calculated and experimental vibrational frequencies, the (SMD)-B3LYP-D3/def2-TZVPD harmonic frequencies were scaled by the factor of 0.9674 as recommended by Kesharwani *et al.*<sup>31</sup> Although application of the scaling factor to the highly anharmonic NH and OH stretch vibrations requires caution: a high-accuracy *ab initio* anharmonic force field study of  $\text{N}_2\text{OH}^+$  showed<sup>23</sup> that for the purposes of this work, the above mentioned scaling of the harmonic frequencies is reasonable. To obtain more accurate relative energies of some isomers, single-point high-level CCSD(T)/def2-TZVPD coupled-cluster computations<sup>32</sup> within a frozen core approximation were additionally conducted.

The natural population analysis partial charges<sup>33,34</sup> were calculated at the (SMD)-B3LYP-D3/def2-TZVPD theoretical level for the species of interest as implemented in Gaussian09,<sup>35</sup> whereas natural resonance theory<sup>36–38</sup> analysis was carried out at the B3LYP/TZ2P level of theory using scalar relativistic (SR) zero-order regular approximation Hamiltonian (core potentials were not used, and the quality of the Becke numerical integration grid was set to the keyword good)<sup>39</sup> in the ADF2016 software suite.<sup>40–42</sup>

(SMD)-B3LYP-D3/def2-TZVPD and CCSD(T)/def2-TZVPD computations were performed using the Gaussian09 software.<sup>35</sup> The def2-TZVPD basis sets were retrieved from the EMSL database.<sup>43,44</sup>

All the compounds were assumed to be in their ground state. The spin-unrestricted formalism was used for both density functional theory (DFT) and CCSD(T) calculations when computing radicals.

## Results of calculations

The gas phase B3LYP-D3/def2-TZVPD calculations of  $\{\text{F}_{11}\}$ -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  $\text{N}_2\text{OH}^+\cdots\text{L}$  and  $\text{NO}_2\text{H}^+\cdots\text{L}$  model systems, where L = Ar, Kr, Xe, CO, or  $\text{SO}_2$ . A wide range of L basicities, which includes the basicity of the  $\{\text{F}_{11}^-\}$  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†).

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

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

$\text{N}_2\text{O}$  described by the N-oxide valence formula,  $\text{N}\equiv\text{N}^+-\text{O}^-$  (Fig. S6, ESI†), has two valence frequencies (Table S1, ESI†),  $\nu_{\text{as}}\text{N}_2\text{O}$  at 2268  $\text{cm}^{-1}$  and  $\nu_{\text{s}}\text{N}_2\text{O}$  at 1285  $\text{cm}^{-1}$ , which can be represented as the characteristic vibrations of the NN and NO stretches, respectively. The bent vibration is at 598  $\text{cm}^{-1}$ . Protonation of  $\text{N}_2\text{O}$  leads to formation of the  $\text{N}\equiv\text{N}-\text{OH}^+$  cation (Fig. S7a, ESI†), with a significant decrease in the NO stretch ( $\sim 250$   $\text{cm}^{-1}$ ) and an increase in the NN stretch (by  $\sim 90$   $\text{cm}^{-1}$ ; Table S2, ESI†) because the N–O and  $\text{N}\equiv\text{N}$  bonds approach the common single and triple bond respectively.

According to vibrational analysis, the solvation of  $\text{N}_2\text{OH}^+$  by Ar, Kr, or Xe weakened the OH bond and strengthened the NO bond (Table S2, ESI†). The dependence of the  $\nu_{\text{NO}}$  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 ( $\text{N}_2\text{O}$ ) $\text{H}^+-\text{L}$  bond is ionic. Nevertheless, the analogous dependences for  $\nu_{\text{OH}}$  and  $\nu_{\text{NN}}$  frequencies deviate from the linear function to a greater extent with the greater basicity of L because a decrease in the frequency of  $\text{OH}^+$  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  $\text{N}_2\text{OH}^+$  is solvated by the stronger bases, CO,  $\text{SO}_2$ , and  $\{\text{F}_{11}^-\}$ , which formed a partially covalent bond with a cation. This situation leads to the formation of a rather asymmetric proton disolvate of the  $\text{L}_1-\text{H}^+\cdots\text{L}_2$  type ( $\text{L}_1 = \text{N}_2\text{O}$ ;  $\text{L}_2 = \text{SO}_2$ ,



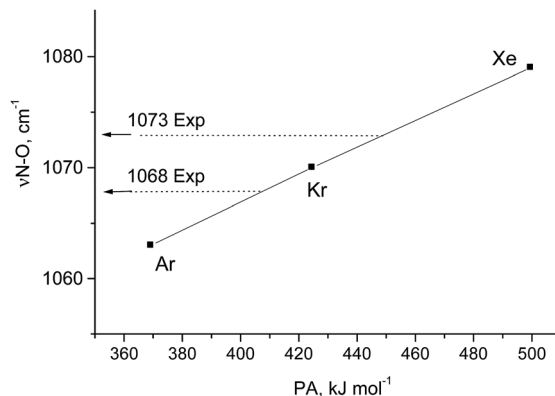


Fig. 2 Dependence of the N–O stretch of  $\text{N}_2\text{O}-\text{H}^+\cdots\text{L}$  on the PA of L atoms. Experimental frequencies are given for comparison.

$\{\text{F}_{11}^-\}$ ) with a further increase in the frequency of the N–O stretch (Table S2, ESI<sup>†</sup>).

### $(\text{NO}_2)\text{H}^+$ cation

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

### $(\text{N}_2\text{O}_4)\text{H}^+$ 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 N–N bond length of  $1.78 \text{ \AA}$ . After protonation, the optimized structure of  $\text{N}_2\text{O}_4\text{H}^+$  (Ic10 in Fig. S4, ESI<sup>†</sup>) showed a significant increase in the N–N distance ( $2.247 \text{ \AA}$ ), which precluded its formation. Solvation of the  $\text{N}_2\text{O}_4\text{H}^+$  cation with such bases as Ar, CO,  $\text{SO}_2$ , or  $\{\text{F}_{11}^-\}$ , reduced the N–N distance down to  $2.179$ ,  $2.079$ ,  $2.023$ , and  $1.909 \text{ \AA}$  respectively, but it was still big enough for the cation to exist. Calculations predicted that unstable  $\text{N}_2\text{O}_4\text{H}^+\cdots\text{L}$  can decompose in the simplest way into a  $(\text{HNO}_3\cdots\text{NO}^+)\cdots\text{L}$  compound (Fig. S4, S5 and Tables S4, S5, ESI<sup>†</sup>). 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 $\text{H}\{\text{F}_{11}\}$ acid

After injection of  $\text{N}_2\text{O}$  into the IR cell-reactor with the sublimed  $\text{H}\{\text{F}_{11}\}$  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  $\text{H}\{\text{F}_{11}\}$ . After vacuum removal of the gaseous  $\text{N}_2\text{O}$ , the band at  $2231 \text{ cm}^{-1}$  persisted, but after fast heating up to  $100 \text{ }^\circ\text{C}$  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  $\text{H}\{\text{F}_{11}\}$  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

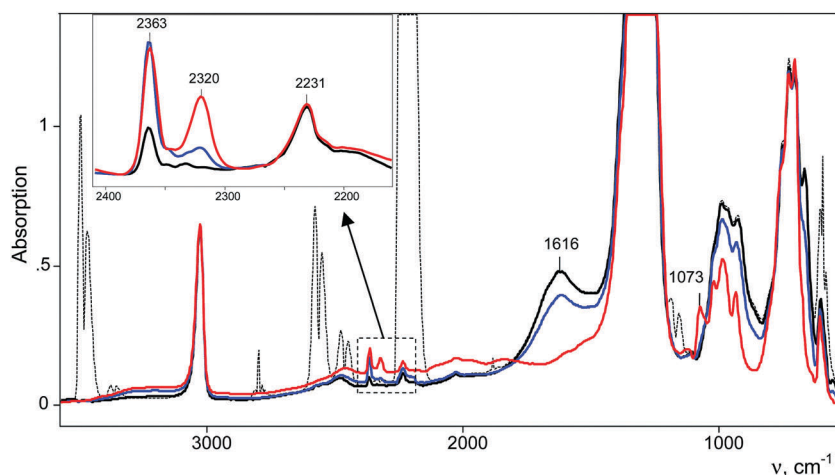


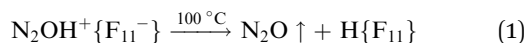
Fig. 3 IR spectra of the compounds formed when  $\text{H}\{\text{F}_{11}\}$  is aged under an atmosphere of  $\text{N}_2\text{O}$  for 2 min (black solid and dashed curves), 1 h (blue curve) and 10 h (red curve). The spectra are shown before (dashed curve) and after subtraction (black solid curve) of the spectrum of gaseous  $\text{N}_2\text{O}$ . The red spectrum was registered after vacuum removal of the gaseous phase.



that bind to the most basic “b” and “c” sites of the  $\{F_{11}^-\}$  anion (hereinafter referred to as  $N_2OH^+_b$  and  $N_2OH^+_c$ ), as is the case for  $H^+CO$  binding to  $\{F_{11}^-\}$ .<sup>3</sup> Simultaneously, the absorption corresponding to the free (unreacted)  $H\{F_{11}\}$  acid decreases and after 8–10 h disappears (judging by the indicative band at  $1616\text{ cm}^{-1}$  of the stretch vibration of the bridged proton in polymeric acid  $[H\{F_{11}\}]_n$ , Fig. 3). In the low-frequency region of the  $N-O(H^+)$  stretches, weak complex bands appeared at  $1068$  and  $1073\text{ cm}^{-1}$ , which correspond to  $N_2OH^+_c$  and  $N_2OH^+_b$ , respectively (Fig. 5).

Fig. 4 shows the intensity dependences of the bands of the NN stretches from  $N_2OH^+_b$  and  $N_2OH^+_c$  ( $A_{NN}$  at  $2321$  or  $2364\text{ cm}^{-1}$  respectively) on the absorption intensity of the acid being used (an intensity decrease at  $1616\text{ cm}^{-1}$ ,  $A_{1616}$ ). The figure shows that the formation of the  $N_2OH^+_b$  and  $N_2OH^+_c$  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  $N_2O$  was removed by evacuation. The cell was sealed and heated to  $100\text{ }^\circ\text{C}$  for 5 min. The IR spectrum shows the emergence of a weak spectrum of gaseous  $N_2O$  from the desorbed  $N_2O$ . It should be noted that the broad band of the bridged proton of the free  $H\{F_{11}\}$  acid at  $1616\text{ cm}^{-1}$  appeared as well. That is, reaction (1) of  $N_2OH^+$  decomposition takes place.



Partial decomposition of  $N_2OH^+$  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  $H\{F_{11}\}$  will have negative intensity.

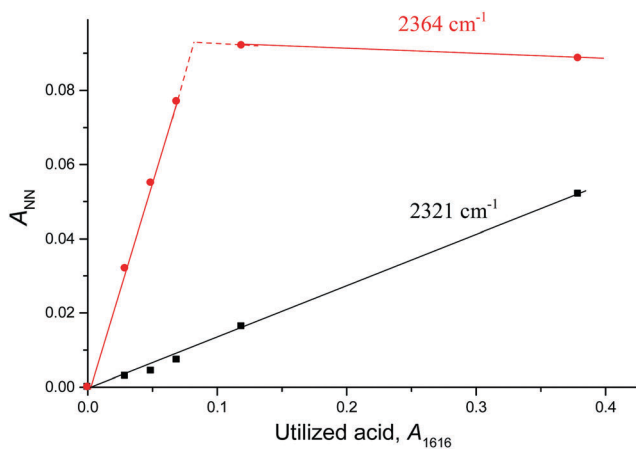


Fig. 4 Dependences of the intensity of the bands of  $\nu_{NN}$  from cations  $N_2OH^+_b$  (at  $2321\text{ cm}^{-1}$ ) and  $N_2OH^+_c$  (at  $2364\text{ cm}^{-1}$ ) on the absorption of the acid being used (is equal to the decrease in intensity of the free acid at  $1616\text{ cm}^{-1}$ ).

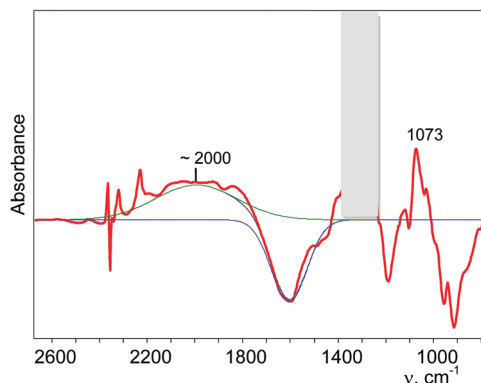


Fig. 5 Determination of the band of the  $O-H^+$  stretch of the  $N_2OH^+$  cation (for details see Fig. S10 in ESI<sup>†</sup>).

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

### Interaction of $NO_2$ with the $H\{F_{11}\}$ acid

Interaction of gaseous  $NO_2$  with a thin film of the amorphous acid on the Si windows of the IR cell reactor results in a decreasing absorption band of the bridged proton of the  $H\{F_{11}\}$  acid at  $1616\text{ cm}^{-1}$  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  $NO_2H^+ \cdots L$  type compounds predicted by calculations (Table S3, ESI<sup>†</sup>) but show bands of the stretch vibrations in the frequency region of  $2300\text{--}2400\text{ cm}^{-1}$  belonging to the other compounds. One of these bands at  $2364\text{ cm}^{-1}$  coincides exactly with that of  $N_2OH^+_c$ . Moreover, as the reaction of  $NO_2$  with  $H\{F_{11}\}$  proceeded, the band of the NN stretch at  $2223\text{ cm}^{-1}$  of gaseous  $N_2O$  emerged and increased in intensity (Fig. 6, inset). The dependence of the intensity of the band at  $2364\text{ cm}^{-1}$  on that of  $2223\text{ cm}^{-1}$  is strictly proportional (Fig. 7); this result confirmed the joint formation of  $N_2OH^+_c$  and  $N_2O$  in the course of the secondary reactions that take place between the initially formed  $NO_2H^+_c$  and gaseous  $NO_2$ .

A distinctive band of the second compound at  $2334\text{ cm}^{-1}$  is typical in terms of frequency for the NN stretch of the  $N_2OH^+$  cation but did not coincide with that of  $N_2OH^+_b$  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  $3560\text{ cm}^{-1}$  (Fig. 6) which, without a doubt, belongs to OH stretch vibrations (IR spectra did not show the bands from the OH stretches of the  $H_3O^+$  cation<sup>4</sup>). The dependence of the intensity of the band at  $2334\text{ cm}^{-1}$  on that of  $\nu_{OH}$  at  $3560\text{ cm}^{-1}$  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  $H\{F_{11}\}$  acid (precipitated in liquid HCl during its synthesis) was aged in an atmosphere of  $NO_2$ . At a low partial pressure of  $NO_2$  (*ca.*  $0.2\text{ atm}$ ) presumably  $N_2OH^+_c$  is formed, whereas at a higher partial pressure (*ca.*  $0.8\text{ atm}$ ) the second compound mainly is formed (Fig. 9a). The only new band detected in the spectrum of the second compound





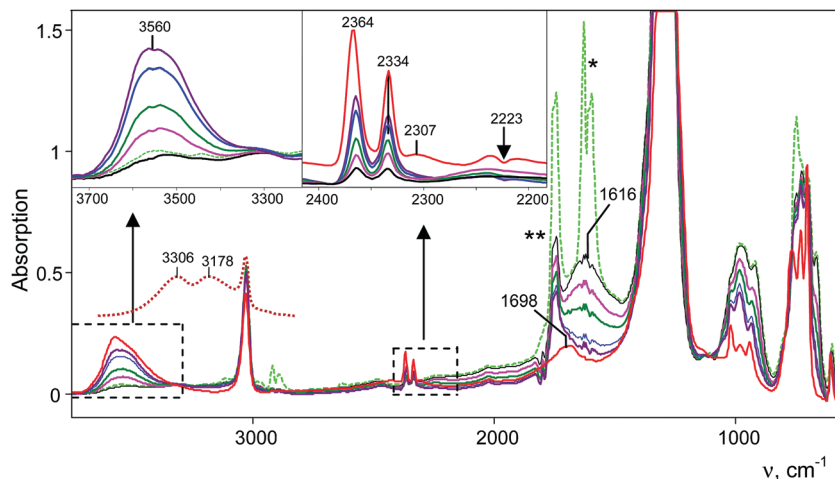


Fig. 6 IR spectra of the reaction products of a gas mixture  $\text{NO}_2 + \text{N}_2\text{O}_4$  with the  $\text{H}\{\text{F}_{11}\}$  acid. Reaction times are 4 min (green, black curves), 3 h (purple curve) and 24 h (red curve). Spectra are shown without (green curve) and with digital subtraction (full for  $\text{N}_2\text{O}$  and partial for  $\text{N}_2\text{O}_4$ ) of the spectrum of the gaseous mixture (dark purple curve). The red spectrum was registered after vacuum removal of the gaseous mixture.  $\nu_{\text{as}}\text{NO}_2$  of  $\text{NO}_2$  is marked with \*, and  $\nu_9$  of  $\text{N}_2\text{O}_4$  is marked with \*\*. The spectrum of  $\text{H}_3\text{O}^+\{\text{F}_{11}^-\}$  in the frequency region of OH stretches is given for comparison (dotted brown curve).

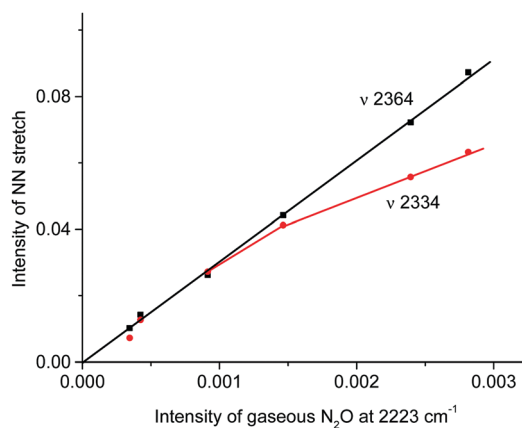


Fig. 7 Dependences of the intensity of the  $\text{N}\equiv\text{N}$  stretch of the  $\text{N}_2\text{OH}^+$  cation on the intensity of the band at  $2223\text{ cm}^{-1}$  of the formed gaseous  $\text{N}_2\text{O}$ .

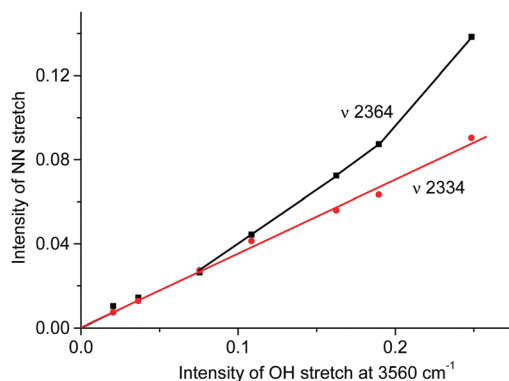


Fig. 8 Dependences of intensity of the  $\text{N}\equiv\text{N}$  stretch of the  $\text{N}_2\text{OH}^+$  cation on the intensity of the band of the OH stretch at  $3560\text{ cm}^{-1}$ .

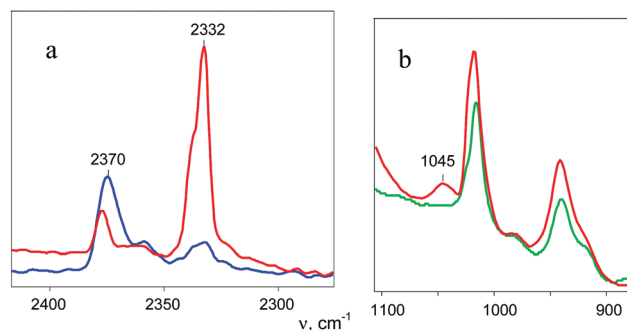


Fig. 9 ATR IR spectra of  $\text{N}_2\text{OH}^+\text{c}\{\text{F}_{11}^-\}$  (blue curve) and  $\text{N}_2\text{OH}_{\text{free}}^+\{\text{F}_{11}^-\}$  (red curve) in comparison with the spectrum of the salt  $\text{Cs}\{\text{F}_{11}^-\}$  (green curve), which allowed identification of the  $\text{N}-\text{O}(\text{H}^+)$  stretch at  $1045\text{ cm}^{-1}$  for  $\text{N}_2\text{OH}_{\text{free}}^+$ .

is at  $1045\text{ cm}^{-1}$ , which is common for the  $\text{N}-\text{O}(\text{H})$  stretch frequency (Fig. 9b and Table S2, ESI†).

This 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  $\text{N}_2\text{O}$ . Thus, the second compound is the salt of the  $\text{N}_2\text{OH}^+$  cation with a free OH bond (further denoted as  $\text{N}_2\text{OH}_{\text{free}}^+$ ), which is decomposed by water with  $\text{N}_2\text{O}$  elimination.

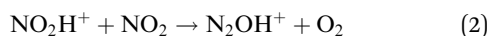
Finally, the third band in the frequency range of the NN stretch appears at  $2307\text{ cm}^{-1}$  after long aging of the sample under an atmosphere of  $\text{NO}_2$  (more than 24 h, Fig. 6). We propose that it emerges due to water vapor penetration. We verified this idea by introducing water vapor into the IR cell along with the  $\text{N}_2\text{OH}^+\{\text{F}_{11}^-\}$  salt and observed rapid disappearance of the bands of the NN stretches of the  $\text{N}_2\text{OH}^+$  and  $\text{N}_2\text{OH}_{\text{free}}^+$  cations, but the band at  $2307\text{ cm}^{-1}$  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  $\text{N}_2\text{OH}_b^+$  and  $\text{N}_2\text{OH}_c^+$  cations (Table 1) with the calculated spectra (Table S2, ESI†) shows that these cations belong to the  $L_1\text{-H}^+\cdots L_2$  type, where  $L_1 = \text{N}_2\text{O}$  and  $L_2 = \{\text{F}_{11}^-\}$  anion with “b” and “c” basic sites. These empirical spectra show the greatest congruence with those calculated for the  $\text{N}_2\text{OH}^+\cdots\text{Kr}$  and  $\text{N}_2\text{OH}^+\cdots\text{Xe}$  solvates (Table S2, ESI†); in particular, the  $\nu\text{N-O}$  frequency almost coincides with that of  $\text{N}_2\text{OH}^+\cdots\text{Kr}$  (Fig. 2). This result implies that an “effective” PA of  $\{\text{F}_{11}^-\}$  in the solid  $\text{N}_2\text{OH}^+\{\text{F}_{11}^-\}$  salt is close to that of the Kr atom. Moreover, the positive charge and electron density redistribution over the  $\text{N}\equiv\text{N-O}$  group of the  $\text{N}_2\text{OH}^+\cdots\text{Kr}$  cation, as well as the geometric parameters of these groups, determined by means of calculations, should be very close to those of  $\text{N}_2\text{OH}_b^+$  and  $\text{N}_2\text{OH}_c^+$ . Thus, these cations can be described as having the NNO angle close to  $180^\circ$  with the triple  $\text{N}\equiv\text{N}$  (*ca.* 1.001 Å) and single  $\text{N-O(H}^+)$  bonds (*ca.* 1.252 Å) in accordance with the N oxide valence formula  $\text{N}\equiv\text{N}^+\text{-OH}$ . On the other hand, the O–H stretch at *ca.* 2000  $\text{cm}^{-1}$  indicates strong H-bonding with the  $\{\text{F}_{11}^-\}$  anion having the positive charge mainly on the H atom (Scheme 1).

Attempts to protonate  $\text{NO}_2$  led to an unexpected result: the spectrum of the cation radical  $\text{NO}_2\text{H}^{\bullet+}$  predicted by calculations (Table S3, ESI†) is not registered, but the spectrum of  $\text{N}_2\text{OH}^+$  cations appeared. Obviously, there is a rapid transition from  $\text{NO}_2\text{H}^+$  to the  $\text{N}_2\text{OH}^+$  cation, which can only take place *via* reaction (2)

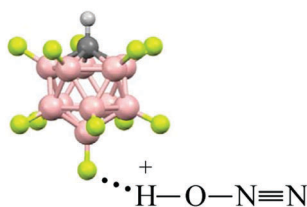


because the formation of other nitrogen oxides was not registered by IR spectroscopy either in the solid phase or in the gas phase. Unfortunately,  $\text{O}_2$  generated by reaction (2) is not detected by IR spectroscopy. Eqn (2) is suggestive of the formation of an intermediate: the protonated dimer of nitrogen dioxide,  $\text{N}_4\text{O}_2\text{H}^+$ . This cation can also be formed by the direct

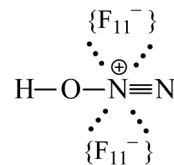
**Table 1** Some frequencies of  $\text{N}_2\text{OH}^+$  cations in solid phases with the  $\{\text{F}_{11}^-\}$  counter ion

Cation	$\nu\text{OH}$	$\nu\text{NN}$	$\nu\text{NO}$	$\delta\text{NOH}$
$\text{N}_2\text{OH}_b^+$	~2000	2321	1073	<sup>a</sup>
$\text{N}_2\text{OH}_c^+$	~2000	2364	1060	<sup>a</sup>
$\text{N}_2\text{OH}_{\text{free}}^+$	3560	2334	1045	1698

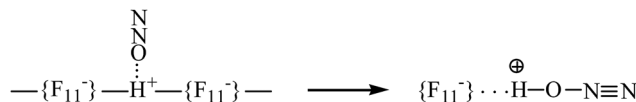
<sup>a</sup> Not identified.



**Scheme 1** Representative structure of the  $\text{N}_2\text{OH}_c^+$  cation in its salt with the  $\{\text{F}_{11}^-\}$  anion.

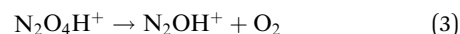


**Scheme 2** Schematic presentation of  $\text{N}_2\text{OH}_{\text{free}}^+$  in its salt with the  $\{\text{F}_{11}^-\}$  anion.



**Scheme 3** Illustration of  $\text{N}_2\text{O}$  physically adsorbed by the surface Brønsted centers of the  $\text{H}\{\text{F}_{11}\}$  acid (left), followed by the proton transfer to  $\text{N}_2\text{O}$ .

protonation of  $\text{N}_4\text{O}_2$ , which is present in amounts comparable with those of  $\text{NO}_2$  in the gaseous mixture. Unstable  $\text{N}_4\text{O}_2\text{H}^+$  further decomposes into  $\text{N}_2\text{OH}^+$  in accordance with eqn (3)



It was a surprise that one of the two  $\text{N}_2\text{OH}^+$  cations formed in reactions (2) or (3) is  $\text{N}_2\text{OH}_{\text{free}}^+$  with a free OH group, which is not H-bonded to the  $\{\text{F}_{11}^-\}$  anion. This means that  $\text{N}_2\text{OH}_{\text{free}}^+$  exactly matches the N oxide valence formula  $\text{N}\equiv\text{N}^+\text{-OH}$  with the positive charge located on the central N atom. The stretch O–H frequency of  $\text{N}_2\text{OH}_{\text{free}}^+$  is higher ( $3560\text{ cm}^{-1}$ ) than that of the free cation in vacuum, both calculated ( $3332\text{ cm}^{-1}$ ) and empirically determined ( $3331\text{ cm}^{-1}$ ).<sup>12,13</sup> This means that the interaction of  $\text{N}_2\text{OH}_{\text{free}}^+$  with the neighboring  $\{\text{F}_{11}^-\}$  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  $\text{N}_2\text{OH}^+$  in vacuum. Thus,  $\text{N}_2\text{OH}_{\text{free}}^+$  is an unusual representative of a pure Lewis acid with a covalent OH group.

Cation radical  $\text{NO}_2\text{H}^{\bullet+}$ , formed in the first step of  $\text{NO}_2$  protonation with  $\text{H}\{\text{F}_{11}\}$ , according to calculations (Table S5, ESI†), is stable. Nevertheless, as experiments showed, it has high reactivity and quickly reacts with the next  $\text{NO}_2$  molecule (eqn (2)) forming an unstable intermediate,  $\text{N}_2\text{O}_4\text{H}^+$ . According to calculations, the instability of  $\text{N}_2\text{O}_4\text{H}^+$  is caused by extension of the N–N bond up to 2.247 Å. The simplest route of its decomposition is formation of the  $\text{HNO}_3\text{-NO}^+$  solvate (Fig. S4, S5 and Table S5 in ESI†). In contrast, the experiment shows that decomposition of  $\text{N}_2\text{O}_4\text{H}$  proceeds *via* eqn (3) to  $\text{N}_2\text{OH}^+ + \text{O}_2$ .

The fact that there is a proportionality between the amount of the formed  $\text{N}_2\text{OH}_c^+$  and gaseous  $\text{N}_2\text{O}$  (Fig. 2) indicates the existence of an equilibrium  $\text{N}_2\text{OH}_c^+\{\text{F}_{11}^-\} \rightleftharpoons \text{N}_2\text{O} + \text{H}\{\text{F}_{11}\}$ , which, however, is absent between  $\text{N}_2\text{OH}_{\text{free}}^+$  and gaseous  $\text{N}_2\text{O}$ . That is,  $\text{N}_2\text{OH}_{\text{free}}^+$  is formed only through  $\text{N}_2\text{O}_4\text{H}^+$  decomposition.

## Conclusion

Gaseous  $\text{N}_2\text{O}$  and  $\text{NO}_2$  are protonated under ambient conditions with the strongest known solid superacid,  $\text{H}\{\text{F}_{11}\}$ .  $\text{N}_2\text{O}$  is attached



to the H atom of the polymeric  $(\text{H}\{\text{F}_{11}\})_n$  acid at the first stage *via* physical adsorption without breaking the bridge H-bond and proton transfer to the  $\text{N}_2\text{O}$  molecule (Scheme 3, left). The adsorbed  $\text{N}_2\text{O}$  molecules are not desorbed in vacuum at room temperature, but are easily detached at elevated temperatures.

The second stage is the breakage of the  $-\{\text{F}_{11}\}-\text{H}-\{\text{F}_{11}\}-$  hydrogen bridge and proton transfer to the O atom of  $\text{N}_2\text{O}$  (Scheme 3). The formed  $\text{N}_2\text{OH}^+$  cation retains a fairly strong H bond with the  $\{\text{F}_{11}^-\}$  anion, attaching to its “b” or “c” site (Scheme 1). This compound can be regarded as an asymmetric proton disolvate,  $\text{L}_1-\text{H}^+\cdots\text{L}_2$ , with  $\text{L}_1 = \text{N}_2\text{O}$  and  $\text{L}_2 =$  counterion.

Adsorption of  $\text{NO}_2$  on the surface of the  $\text{H}\{\text{F}_{11}\}$  acid did not reveal the IR absorption pattern of physically adsorbed  $\text{NO}_2$  or protonated  $\text{NO}_2$  because the cation radical  $\text{NO}_2\text{H}^+$ , which obviously must be formed, has high reactivity. It quickly interacts with  $\text{NO}_2$  forming an unstable intermediate,  $\text{N}_2\text{O}_4\text{H}^+$ , which decomposes (eqn (3)) forming two types of  $\text{N}_2\text{OH}^+$  cations. The first one is  $\text{N}_2\text{OH}_c^+$  with a common H-bonding to the  $\{\text{F}_{11}^-\}$  ion. The second one,  $\text{N}_2^+\text{OH}_{\text{free}}$ , 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  $\text{N}_2\text{OH}_c^+$  cation is a typical Brønsted superacid, then the second cation,  $\text{N}_2^+\text{OH}_{\text{free}}$ , 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  $\text{N}_2\text{O}$ , just as CO studied earlier, during protonation by the  $\text{H}\{\text{F}_{11}\}$  acid, cannot form a symmetric proton disolvate of the  $\text{L}-\text{H}^+-\text{L}$  type in the solid phase. For this reason, the results of another article [ref. 25]—claiming that  $\text{CO}_2$ , less basic than either  $\text{N}_2\text{O}$  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.

## Acknowledgements

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