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## A combined quantum-chemical and matrix-isolation study on molecular manganese fluorides†‡

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Molecular manganese fluorides were studied using quantum-chemical calculations at DFT and CCSD(T) levels and experimentally by matrix-isolation techniques. They were prepared by co-deposition of IR-laser ablated elemental manganese or manganese trifluoride with F<sub>2</sub> in an excess of Ne, Ar, or N<sub>2</sub> or with neat F<sub>2</sub> at 5–12 K. New IR bands in the Mn–F stretching region are detected and assigned to matrix-isolated molecular MnF<sub>x</sub> (x = 1–3).

### Introduction

Manganese is an essential element for all living creatures and plays a key role in the process of photosynthesis.<sup>1</sup> Beyond that it has gained importance on a laboratory scale as a reagent for quantitative analysis<sup>2</sup> and on an industrial scale as an alloy component.<sup>3</sup> This is mostly due to its high bonding affinity towards oxygen that culminates in the stability of Mn<sub>2</sub>O<sub>7</sub><sup>4</sup> which contains manganese in its highest possible oxidation state +VII. For the stabilization of high positive oxidation states very electronegative ligands are necessary and besides oxygen also fluorine is used.<sup>5</sup> The highest oxidation state of a manganese fluoride is +IV in solid MnF<sub>4</sub>.

In the binary system of manganese and fluorine MnF has gained attention due to the high multiplicity of its <sup>7</sup>Σ<sup>+</sup> ground state. MnF has been studied extensively by theoretical methods<sup>6</sup> as well as experimentally using mass spectrometry,<sup>7</sup> rotational,<sup>8–10</sup> matrix-infrared<sup>11</sup> and electron spin resonance spectroscopy.<sup>12</sup> Commercially available MnF<sub>2</sub> and MnF<sub>3</sub> have been studied in detail in both solid and gaseous forms especially with regard to Jahn–Teller-distortion<sup>12–14</sup> using gas-phase electron diffraction,<sup>15,16</sup> X-ray diffraction,<sup>17,18</sup> neutron scattering,<sup>19</sup> vibrational spectroscopy,<sup>20–22</sup> and mass spectrometry.<sup>7,23</sup> MnF<sub>2</sub> and MnF<sub>3</sub> were thermally evaporated using a Knudsen cell and subsequently deposited in solid argon and neon matrices.<sup>20,21</sup> Another approach to study molecular MnF<sub>x</sub> species is from thermally generated manganese atoms, which were treated with elemental fluorine. MnF, MnF<sub>2</sub> and MnF<sub>3</sub>

were formed, and an IR band obtained in solid Ar at 768.7 cm<sup>−1</sup> was tentatively assigned to “a molecule richer in fluorine than MnF<sub>3</sub>”.<sup>11</sup> MnF<sub>4</sub> is a blue solid, first synthesized in 1961<sup>24</sup> and later employed in the chemical synthesis of elemental fluorine.<sup>25</sup> It has been characterized in the solid state by X-ray diffraction,<sup>26</sup> vibrational spectroscopy<sup>22,27</sup> and magnetic susceptibility measurements.<sup>24,28</sup> Since it cannot be evaporated without decomposition to MnF<sub>3</sub> and F<sub>2</sub><sup>29</sup> the investigation of molecular MnF<sub>4</sub> is challenging. In an earlier study solid MnF<sub>3</sub> was treated with TbF<sub>4</sub> at 700 K and an IR band at 794.5 cm<sup>−1</sup> in the MnF stretching region as well as two weaker bands at 172.9 cm<sup>−1</sup> and 176.6 cm<sup>−1</sup> of the Ar-matrix isolated products were claimed to be molecular MnF<sub>4</sub>.<sup>23</sup> From the appearance of a single band in the Mn–F stretching region a tetrahedral structure was deduced.

The fact that up to now binary fluorides of manganese higher than MnF<sub>4</sub> have not been obtained is remarkable. The heavier homologue technetium forms TcF<sub>6</sub>,<sup>30</sup> while TcF<sub>7</sub> is predicted to be stable,<sup>31</sup> and ReF<sub>7</sub> is well-known.<sup>32</sup> FeF<sub>4</sub> and CrF<sub>5</sub> have been characterized,<sup>33,34</sup> while earlier reports on the existence of CrF<sub>6</sub> were shown to be erroneous.<sup>35</sup> A previous report about the possible existence of manganese pentafluoride taking into account thermochemical data and sterical considerations<sup>36</sup> stimulated us to reinvestigate the higher molecular Mn–F species using quantum-chemical calculations at DFT and CCSD(T) levels and to conduct matrix-isolation experiments in combination with IR spectroscopy.

Instead of thermally evaporating manganese, we have used the IR-laser ablation of elemental manganese to generate more reactive excited manganese atoms, which were co-condensed with fluorine diluted (0.25–3%) in neon, argon or nitrogen and neat fluorine. In addition we report about IR-laser ablation of manganese trifluoride, which has not been described previously.

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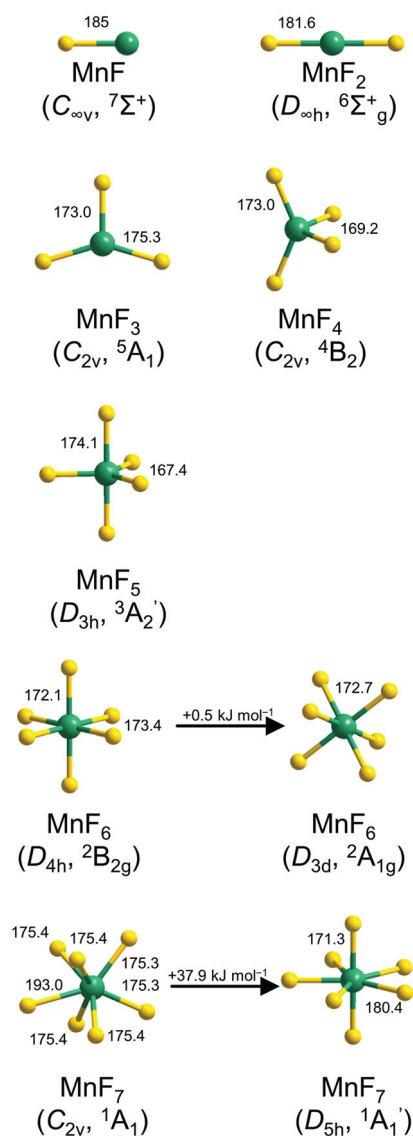


## Results and discussion

### Calculated structures, thermochemistry and vibrational frequencies

Optimized structures for the binary manganese fluorides  $\text{MnF}_x$  ( $x = 1-7$ ) are shown in Fig. 1.

The binary manganese fluorides have a high-spin ground state. The bond length of diatomic  $\text{MnF}$  calculated at the CCSD(T) level by Nhat *et al.* was 185 pm,<sup>6</sup> which is fairly close to our value of 184.3 pm at the DFT level and that obtained experimentally by rotational spectroscopy (183.9 pm).<sup>10</sup>  $\text{MnF}_2$  is computed to be linear with a CCSD(T) bond length of 181.6 pm. Gas phase electron diffraction gave a consistent value of 181.1 pm.<sup>15</sup>  $\text{MnF}_3$  has a distorted trigonal planar structure.



**Fig. 1** Optimized structures of molecular manganese fluorides at the CCSD(T) ( $\text{MnF}$ – $\text{MnF}_5$ ) and DFT levels ( $\text{MnF}_6$  and  $\text{MnF}_7$ ). Selected bond lengths (pm) and angles ( $^\circ$ ) are indicated. For a complete list see also Table S1 in the ESI.†

The quintet ground state shows two longer Mn–F bonds (175.3 pm) and one shorter Mn–F bond (173.0 pm) at the CCSD(T) level, which is in very good agreement with the results from gas phase electron diffraction (175.4 pm and 172.8 pm).<sup>16</sup> According to our CCSD(T) calculations  $\text{MnF}_4$  has a distorted tetrahedral structure ( $C_{2v}$  symmetry) with Mn–F bond lengths of 173.0 pm and 169.2 pm. For  $\text{MnF}_5$  a trigonal bipyramidal minimum structure ( $D_{3h}$  symmetry) with bond lengths of 174.1 pm (Mn– $F_{\text{ax}}$ ) and 167.4 pm (Mn– $F_{\text{eq}}$ ) was computed at the CCSD(T) level. The  $d^1$  electron configuration of manganese in  $\text{MnF}_6$  causes a distortion from a regular octahedral structure which leads to either a structure with  $D_{4h}$ - or  $D_{3d}$ -symmetry. Both isomers are minima on the potential energy surface with the trigonal antiprismatic structure (bond lengths of 172.7 pm) just 0.5 kJ mol<sup>-1</sup> in energy above the tetragonal bipyramidal structure (Mn– $F_{\text{ax}}$  172.1 pm, Mn– $F_{\text{eq}}$  173.4 pm) at the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level. For  $\text{MnF}_7$  also two minimum structures were computed at the DFT level. The regular  $D_{5h}$ -symmetrical pentagonal bipyramidal isomer exhibits Mn– $F_{\text{ax}}$  bond lengths of 171.3 pm and Mn– $F_{\text{eq}}$  bond lengths of 180.4 pm. The monocapped trigonal prismatic isomer revealed four Mn–F bonds of 175.4 pm and two slightly shorter bonds of 175.3 pm, while the seventh fluorine atom is considerably weaker bound with 193.0 pm (Fig. 1). At the CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level the latter isomer is favored in energy by 37.9 kJ mol<sup>-1</sup>. This is in contrast to the computed minimum structure of  $\text{TcF}_7$ <sup>31</sup> and the crystal structure of  $\text{ReF}_7$ <sup>37</sup> which both are (slightly) distorted pentagonal bipyramids. The reason for this disparity could be the smaller radius of the manganese atom compared to technetium and rhenium atoms.

The observability of a transient molecule in a matrix-isolation experiment requires at least a marginal thermochemical stability. This can be assessed by calculating the enthalpy of possible decomposition reactions. Table 1 lists the corres-

**Table 1** Calculated decomposition enthalpies at 0 K,  $\Delta H(0\text{ K}) = \Delta E + \Delta\text{ZPE}$ , of molecular manganese fluorides<sup>a</sup>

| Reaction  | B3LYP      |                               | CCSD(T)             |                               |
|---|------------|-------------------------------|---------------------|-------------------------------|
|   | $\Delta E$ | $\Delta E + \Delta\text{ZPE}$ | $\Delta E$          | $\Delta E + \Delta\text{ZPE}$ |
| $\text{MnF}_7 \rightarrow \text{MnF}_5 + \text{F}_2$            | -394.5     | -399.9                        | -357.5 <sup>b</sup> | —                             |
| $\text{MnF}_7 \rightarrow \text{MnF}_6 + \frac{1}{2}\text{F}_2$ | -271.7     | -275.6                        | -195.3 <sup>b</sup> | —                             |
| $\text{MnF}_7 \rightarrow \text{MnF}_6 + \text{F}$              | -194.1     | -201.1                        | -119.3 <sup>b</sup> | —                             |
| $\text{MnF}_6 \rightarrow \text{MnF}_4 + \text{F}_2$            | -67.9      | -76.5                         | -141.5 <sup>b</sup> | —                             |
| $\text{MnF}_6 \rightarrow \text{MnF}_5 + \frac{1}{2}\text{F}_2$ | -122.8     | -124.3                        | -162.2 <sup>b</sup> | —                             |
| $\text{MnF}_6 \rightarrow \text{MnF}_5 + \text{F}$              | -45.2      | -49.8                         | -86.6 <sup>b</sup>  | —                             |
| $\text{MnF}_5 \rightarrow \text{MnF}_3 + \text{F}_2$            | 217.4      | 206.5                         | 131.7               | 119.9                         |
| $\text{MnF}_5 \rightarrow \text{MnF}_4 + \frac{1}{2}\text{F}_2$ | 54.9       | 47.7                          | 20.2                | 12.9                          |
| $\text{MnF}_5 \rightarrow \text{MnF}_4 + \text{F}$              | 132.5      | 122.2                         | 96.5                | 86.4                          |
| $\text{MnF}_4 \rightarrow \text{MnF}_2 + \text{F}_2$            | 405.0      | 397.8                         | 304.1               | 295.3                         |
| $\text{MnF}_4 \rightarrow \text{MnF}_3 + \frac{1}{2}\text{F}_2$ | 162.5      | 158.7                         | 111.4               | 107.0                         |
| $\text{MnF}_4 \rightarrow \text{MnF}_3 + \text{F}$              | 240.1      | 233.2                         | 187.7               | 180.5                         |
| $\text{MnF}_3 \rightarrow \text{MnF}_2 + \frac{1}{2}\text{F}_2$ | 242.6      | 239.1                         | 192.6               | 188.3                         |
| $\text{MnF}_3 \rightarrow \text{MnF}_2 + \text{F}$              | 320.2      | 313.6                         | 268.9               | 261.8                         |

<sup>a</sup> Values in kJ mol<sup>-1</sup>. <sup>b</sup> CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ.



**Table 2** Calculated and experimentally observed IR wavenumbers of Mn–F stretching modes of molecular manganese fluorides<sup>a</sup>

| Molecule   | Mode                        | Calc. |       |                    |       | Exp.                                     |  |                    |
|--|-----------------------------|-------|-------|--------------------|-------|--|--|--------------------|
|  |                             | B3LYP |       | CCSD(T)            |       | Ne                                       | Ar   | N <sub>2</sub>     |
| MnF ( <i>C</i> <sub>∞v</sub> , <sup>7</sup> Σ <sup>+</sup> )                           | Σ <sup>+</sup>              | 607.7 | (134) | 605.9 <sup>b</sup> | —     | 608.5 <sup>c</sup>                       | 589.2 <sup>c</sup><br>588.6 <sup>d</sup>   | 585.8 <sup>c</sup> |
| MnF <sub>2</sub> ( <i>D</i> <sub>∞h</sub> , <sup>6</sup> Σ <sup>+</sup> <sub>g</sub> ) | Σ <sup>-</sup> <sub>u</sub> | 723.5 | (237) | 721.3              | (209) | 721.6 <sup>c</sup><br>722.1 <sup>e</sup> | 699.6 <sup>c</sup><br>700.1 <sup>e</sup><br>699 <sup>d</sup>   |                    |
| MnF <sub>3</sub> ( <i>C</i> <sub>2v</sub> , <sup>5</sup> A <sub>1</sub> )              | A <sub>1</sub>              | 646.1 | (9)   | 656.7              | (15)  | 657.1 <sup>c</sup>                       | 643.7 <sup>c</sup><br>644 <sup>g</sup>   |                    |
|  | A <sub>1</sub>              | 720.9 | (126) | 729.9              | (134) | 726.9 <sup>c</sup><br>728 <sup>g</sup>   | 711.2 <sup>c</sup><br>712 <sup>g</sup><br>711 <sup>d</sup>   |                    |
|  | B <sub>2</sub>              | 764.2 | (256) | 779.3              | (287) | 773.4 <sup>c</sup><br>774 <sup>g</sup>   | 711.2 <sup>f</sup><br>758.7 <sup>c</sup><br>759 <sup>g</sup><br>758 <sup>d</sup><br>758.5 <sup>f</sup> |                    |
| MnF <sub>4</sub> ( <i>C</i> <sub>2v</sub> , <sup>4</sup> B <sub>2</sub> )              | A <sub>1</sub>              | 675.0 | (18)  | 681.5              | (13)  |  |  |                    |
|  | A <sub>1</sub>              | 749.3 | (85)  | 755.5              | (83)  |  |  |                    |
|  | B <sub>1</sub>              | 752.3 | (261) | 777.9              | (299) |  |  | 768.7 <sup>d</sup> |
|  | B <sub>2</sub>              | 792.8 | (123) | 800.0              | (105) |  |  | 794.5 <sup>f</sup> |
| MnF <sub>5</sub> ( <i>D</i> <sub>3h</sub> , <sup>3</sup> A <sub>2</sub> )              | A <sub>2</sub> '            | 742.7 | (299) | 768.5              | (331) |  |  |                    |
|  | E'                          | 816.9 | (272) | 824.4              | (235) |  |  |                    |

<sup>a</sup> Values in cm<sup>-1</sup>, IR intensities in km mol<sup>-1</sup> in parentheses. <sup>b</sup> Ref. 6. <sup>c</sup> This work. <sup>d</sup> Ref. 11. <sup>e</sup> Ref. 20. <sup>f</sup> Ref. 23. <sup>g</sup> Ref. 21.

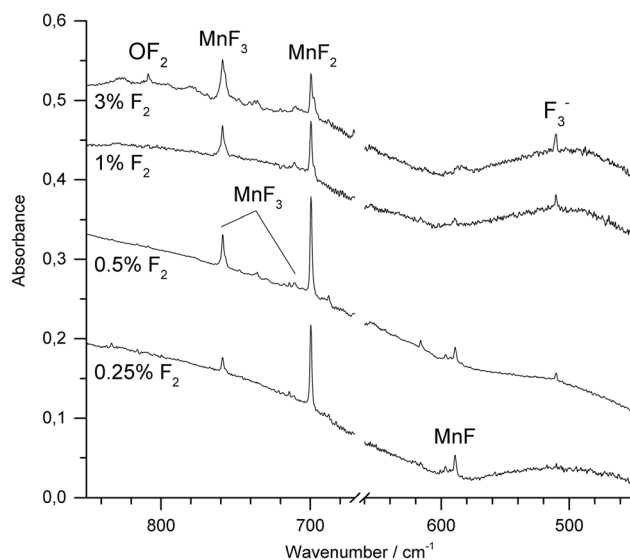
ponding reaction enthalpies for the optimized manganese fluorides.

The decomposition of MnF<sub>7</sub> and MnF<sub>6</sub> is strongly exothermic at all considered pathways including concerted elimination of F<sub>2</sub>, bimolecular reaction and homolytic bond fission. For MnF<sub>5</sub> however the decomposition channels are computed to be endothermic at the CCSD(T) level. Thus, it should be possible to obtain molecular MnF<sub>5</sub> under appropriate conditions, for example in matrix-isolation experiments. However, Δ*G* (298.15 K) for the gas phase reaction MnF<sub>5</sub> → MnF<sub>4</sub> + ½F<sub>2</sub> is calculated to be -12.2 kJ mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVTZ level, so molecular MnF<sub>5</sub> is not stable at ambient temperatures in the gas phase. Considering that sublimation enthalpies are usually smaller for the higher fluorides, MnF<sub>5</sub> is most likely also not stable in the condensed phase. The value of Δ*H*(0 K) = 107.0 kJ mol<sup>-1</sup> obtained for the decomposition MnF<sub>4</sub> → MnF<sub>3</sub> + ½F<sub>2</sub> also suggests a low thermal stability of molecular MnF<sub>4</sub>, which is consistent with the reported vapor pressure of F<sub>2</sub> over solid MnF<sub>4</sub> at room temperature.<sup>29</sup>

Vibrational spectra of the manganese fluorides were calculated at the DFT (MnF–MnF<sub>7</sub>) and CCSD(T) levels (MnF–MnF<sub>5</sub>). The corresponding Mn–F stretching wavenumbers for MnF–MnF<sub>5</sub> are listed and compared to experimentally observed IR bands in Table 2. Calculated IR wavenumbers of Mn–F stretching modes for MnF<sub>6</sub> and MnF<sub>7</sub> are listed in Table S2.‡

### Matrix-isolation experiments

Molecular manganese fluorides were generated by IR-laser (λ = 1064 nm) ablation of a rotating elemental manganese target and co-condensed with fluorine diluted (0.25–3%) in neon or



**Fig. 2** IR spectra in the 450–850 cm<sup>-1</sup> region of the Ar matrix-isolated (12 K) reaction products of laser ablated manganese atoms in the presence of F<sub>2</sub> (0.25–3%) after 1 h of deposition. The region of the bending mode of atmospheric CO<sub>2</sub> (660–670 cm<sup>-1</sup>) was omitted for a better representation.

argon. After deposition of the sample new IR absorptions in the Mn–F stretching region were observed. Fig. 2 shows spectra obtained after deposition of the reaction products of manganese atoms with varying concentrations of F<sub>2</sub> in Ar. The most intense band obtained with fluorine concentrations up to 1%, observed at 699.6 cm<sup>-1</sup> in Ar and 721.6 cm<sup>-1</sup> in Ne,



respectively (ESI; Fig. S1<sup>†</sup>), is associated with the  $\Sigma_u^-$ -mode of  $\text{MnF}_2$ . Bands of  $\text{MnF}_3$  were observed at  $758.7\text{ cm}^{-1}$  and  $711.2\text{ cm}^{-1}$  in Ar and at  $773.4\text{ cm}^{-1}$  and  $726.9\text{ cm}^{-1}$  in Ne, respectively. These values agree very well with those from experiments of thermally evaporated manganese difluoride and trifluoride, respectively.<sup>20,21</sup> While the intensity of the band due to  $\text{MnF}_2$  increased going from 0.25% to 0.5%  $\text{F}_2$  and then decreased with higher fluorine content, the intensity of the bands due to  $\text{MnF}_3$  increased steadily. Also the anti-symmetric stretching band of  $[\text{F}_3]^-$  has been observed at  $510.1\text{ cm}^{-1}$ . This anion has been shown to be formed from  $\text{F}^-$  and a  $\text{F}_2$  molecule during the deposition process, where the  $\text{F}^-$  anion arises from a fluorine atom by electron capture in the plasma plume of an IR-laser ablated metal.<sup>38,39</sup> A decrease in intensity with increasing fluorine concentration was observed for the band at  $589.2\text{ cm}^{-1}$ , which is assigned to diatomic  $\text{MnF}$ , which is in excellent agreement with a previous report.<sup>11</sup> Its counterpart in Ne was observed at  $608.5\text{ cm}^{-1}$  (ESI; Fig. S1<sup>†</sup>). This wavenumber is consistent with an estimated value of  $612.0\text{ cm}^{-1}$  obtained by rotational spectroscopy<sup>40</sup> considering the red-shift of transition metal monofluoride bands experienced in solid noble gases.<sup>41</sup> To the best of our knowledge this is the first report about  $\text{MnF}$  isolated in a neon matrix. It is noteworthy that IR-laser ablation of elemental manganese in the presence of fluorine did not produce any higher fluoride than  $\text{MnF}_3$ . Irradiation of Ar-isolated  $\text{F}_2$  molecules with  $\lambda = 455 \pm 10\text{ nm}$  is proved to produce reactive F-atoms, which are subject to a restricted movement within the solid Ar matrix, and thus may react with adjacent molecules such as  $\text{MnF}_3$ . However, even this photolysis of the deposit failed to produce higher fluorides of manganese.

When neat fluorine was used as matrix gas, several metal dependent absorptions could also be observed within Mn-F stretching range between  $730\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  (ESI; Fig. S2<sup>†</sup>). However, these absorptions were broad and relatively weak in intensity, and their assignment appeared to be difficult. Band broadening and overlapping features were also observed using  $\text{N}_2$  or 1%  $\text{F}_2$  in  $\text{N}_2$  together with IR-laser ablated manganese atoms (ESI; Fig. S3<sup>†</sup>). This result is most likely due to the presence of several matrix sites. However, based on its behavior upon annealing and photolysis a band at  $585.8\text{ cm}^{-1}$  in solid  $\text{N}_2$  could be unambiguously assigned to molecular  $\text{MnF}$ .

We have also conducted IR-laser ablation experiments using a pressed target pellet made of  $\text{MnF}_3$ . Very recently we reported about the laser ablation of alkali metal fluorides,<sup>42</sup> but, to the best of our knowledge, IR-laser ablation of solid transition metal fluorides has not yet been explored. Molecular  $\text{MnF}_3$  generated from a solid  $\text{MnF}_3$  target was first co-condensed with an excess of Ne at 5 K (Fig. 3) and produced bands at  $773.4\text{ cm}^{-1}$  and  $726.9\text{ cm}^{-1}$ . The presence of  $\text{MnF}_2$  ( $\Sigma_u^-$ :  $721.6\text{ cm}^{-1}$ ) indicates some decomposition of  $\text{MnF}_3$  in the plasma plume, probably by F-atom elimination.

When Ar was used as matrix gas (Fig. 4), the band for  $\text{MnF}_2$  shifts to  $699.6\text{ cm}^{-1}$  and those of  $\text{MnF}_3$  to  $758.7\text{ cm}^{-1}$  and  $711.2\text{ cm}^{-1}$ . Additionally, the weaker third Mn-F stretching

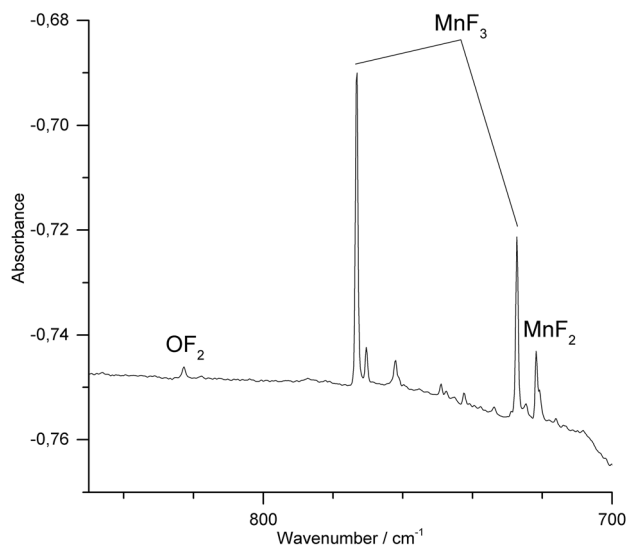


Fig. 3 IR spectrum in the  $700\text{--}850\text{ cm}^{-1}$  region of the Ne matrix-isolated (5 K) products of laser ablated solid  $\text{MnF}_3$  after 15 min of deposition.

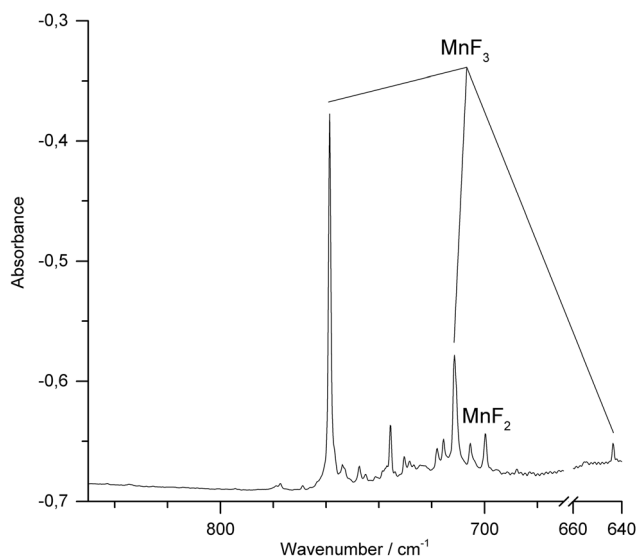
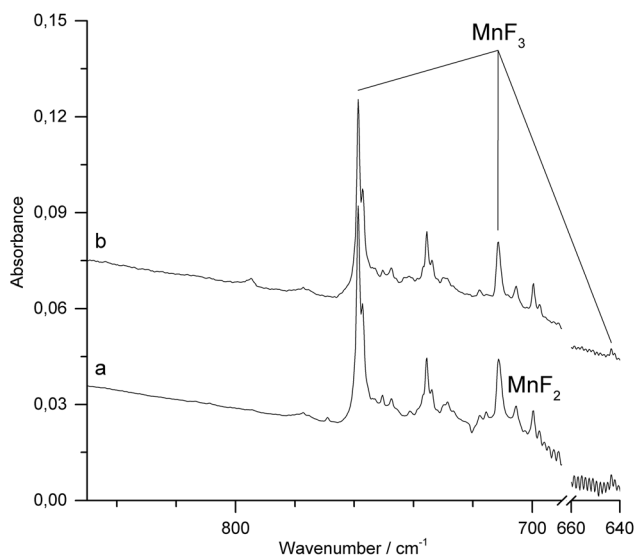


Fig. 4 IR spectrum in the  $640\text{--}850\text{ cm}^{-1}$  region of Ar matrix-isolated (12 K) products of laser ablated solid  $\text{MnF}_3$  after 15 min of deposition. The region of the bending mode of atmospheric  $\text{CO}_2$  ( $660\text{--}670\text{ cm}^{-1}$ ) was omitted for a better representation.

band of  $\text{MnF}_3$  was observed at  $643.7\text{ cm}^{-1}$ . A sharp band observed at  $735.7\text{ cm}^{-1}$  could not be assigned to a mono-nuclear  $\text{MnF}_2$  or  $\text{MnF}_3$  species. This band was previously also observed by the thermal evaporation of solid  $\text{MnF}_3$  and tentatively assigned to a fluorine bridged dimer.<sup>11</sup> In addition, traces of oxygen containing species such as  $\text{OF}_2$  and  $\text{MnO}_3\text{F}^{43-45}$  were detected (ESI; Fig. S4 and S5<sup>†</sup>). Although the target was prepared and fixed to the target holder under inert conditions, some superficial hydrolysis could probably not be





**Fig. 5** IR spectra in the 640–850  $\text{cm}^{-1}$  region of Ar matrix-isolated (12 K) products of laser ablated solid  $\text{MnF}_3$  in the presence of  $\text{F}_2$  (1%). (a) After 15 min of deposition. (b) After 15 min of  $\lambda = 455 \pm 10$  nm irradiation. The region of the bending mode of atmospheric  $\text{CO}_2$  (660–670  $\text{cm}^{-1}$ ) was omitted for a better representation.

prevented during the preparation of the target. The oxygen species  $\text{OF}_2$  and  $\text{MnO}_3\text{F}$  might then have been formed in the plasma plume from the products of this hydrolysis.

IR-laser ablation of solid  $\text{MnF}_3$  was also carried out in the presence of fluorine (1%  $\text{F}_2$  in Ar). Apart from some line broadening, the spectrum (Fig. 5a and ESI; Fig. S6†) is very similar to that obtained without fluorine (Fig. 4). After photolysis ( $\lambda = 455 \pm 10$  nm) a weak feature at 795  $\text{cm}^{-1}$  appeared, which did not grow further with prolonged photolysis (Fig. 5b).

The carrier of this weak band is difficult to assign. A single IR band in the Mn–F stretching region at 794.5  $\text{cm}^{-1}$  was previously obtained in solid Ar from the vaporization of a mixture of  $\text{MnF}_3$  and  $\text{TbF}_4$  at 700 K and assigned to molecular  $\text{MnF}_4$ .<sup>23</sup> From their observation, the authors inferred a tetrahedral structure of molecular  $\text{MnF}_4$ . However, the presence of a single Mn–F stretching band is not in agreement with the calculated  $C_{2v}$  structure of  $\text{MnF}_4$  (Fig. 1), for which at least three strong Mn–F stretching bands are predicted (Table 2). The previous assignment of molecular  $\text{MnF}_4$  to a single Mn–F stretching band at 794.5  $\text{cm}^{-1}$  is therefore questionable, and the carrier of the strong IR band obtained in these experiments remains unknown.

## Experimental and theoretical methods

### Matrix-isolation experiments

**CAUTION:** Appropriate safety precautions should be taken into account when handling pure fluorine and metal fluorides. All equipment has to be adequately pretreated with fluorine prior to use. Note that sudden freezing of samples in metal cylinders

to liquid nitrogen temperatures is potentially dangerous. The suitability of metal cylinders for such a cooling procedure should be proven and the cylinders should always be leak tested at liquid nitrogen temperature prior to filling with poisonous samples. The setup for matrix-isolation and IR-laser ablation experiments has been described in detail previously.<sup>35</sup> The 1064 nm fundamental of a Nd:YAG laser was focused onto a freshly sanded rotating manganese (chemPUR, 99.99%) target or target pellets made of  $\text{MnF}_3$  (Alfa Aesar, 98%). Gaseous mixtures of various concentrations (0.25–100%) of fluorine (Solvay Fluor AG, 99.998%) in neon (Air Liquide, 99.999%), argon (SWF, 99.999%) and nitrogen (Linde, 99.999%) were prepared using a fluorine cylinder ( $V = 1000$   $\text{cm}^3$ , thick-walled stainless steel,  $p_{298\text{ K}} < 1$  bar) cooled to 77 K to freeze out less volatile impurities such as traces of HF and  $\text{CO}_2$ . These mixtures were then co-condensed together with the IR-laser ablated species for 45–60 min onto a CsI cold window cooled to 5 K (Ne matrices) or 12 K (Ar and  $\text{F}_2$ ). Pure fluorine matrices were deposited onto a protective layer of argon to prevent oxidation of the cold window material. FTIR spectra were recorded at a resolution of 0.5  $\text{cm}^{-1}$  on a Bruker Vertex 70 spectrometer equipped with a KBr beam splitter using a liquid nitrogen cooled mercury cadmium telluride (LN-MCTB) detector. A common IR band observed in all spectra of such experiments using IR-laser ablated metal atoms and fluorine is due to the  $[\text{F}_3]^-$  anion at 510.1  $\text{cm}^{-1}$  (Ar), 517.2  $\text{cm}^{-1}$  ( $\text{N}_2$ ), or 524.6  $\text{cm}^{-1}$  (Ne), respectively.<sup>46</sup> As no isotopic splitting of the IR bands of both the monoisotopic manganese and fluorine elements can be observed, any assignment of bands of binary manganese and fluorine species mainly relies on reliably calculated spectra and meaningful variations of experimental conditions.

### Quantum-chemical calculations

Structures of the manganese fluorides  $\text{MnF}_x$  ( $x = 1-7$ ) displayed in Fig. 1 were fully optimized at the DFT level using the B3LYP functional<sup>47-49</sup> in conjunction with the aug-cc-pVTZ basis sets for fluorine<sup>50</sup> and manganese,<sup>51</sup> and considering all reasonable spin multiplicities. Subsequent optimizations at the CCSD(T) level were carried out for the ground states of  $\text{MnF}_x$  ( $x = 2-5$ ). Harmonic frequencies were calculated for stationary points on the potential energy surface. The DFT calculations were performed with Gaussian09<sup>52</sup> and CFOUR<sup>53</sup> was used for the coupled-cluster calculations.

## Conclusion

For more than 50 years solid  $\text{MnF}_4$  has been the highest experimentally known manganese fluoride, but experimental data about its molecular structure are still missing. Quantum-chemical calculations at the CCSD(T) level predict molecular  $\text{MnF}_4$  to be stable against its decomposition according to  $\text{MnF}_4 \rightarrow \text{MnF}_3 + \frac{1}{2}\text{F}_2$  by  $\Delta H(0\text{ K}) = 107$   $\text{kJ mol}^{-1}$ . The corresponding decomposition route for the unprecedented  $\text{MnF}_5$  ( $\text{MnF}_5 \rightarrow \text{MnF}_4 + \frac{1}{2}\text{F}_2$ ) is found to be only marginally endothermic.



mic by  $\Delta H(0\text{ K}) = 12.9\text{ kJ mol}^{-1}$ . Molecular  $\text{MnF}_6$  and  $\text{MnF}_7$  are unstable with respect to their decomposition to lower manganese fluorides. The reaction of IR-laser ablated manganese atoms with elemental fluorine diluted in neon, argon and nitrogen and neat fluorine was studied. The IR analysis of the matrix-isolated products at 5–12 K revealed the formation of molecular  $\text{MnF}$ ,  $\text{MnF}_2$  and  $\text{MnF}_3$ . Molecular  $\text{MnF}_3$  has alternatively been produced and matrix-isolated by IR-laser ablation of a solid manganese trifluoride target. Attempts to detect IR bands of a higher manganese fluoride such as  $\text{MnF}_4$  or  $\text{MnF}_5$  by carrying out these experiments in the presence of elemental fluorine or by additional UV photolysis of the deposits failed. The presented results cast doubt on previous reports about the formation of such higher molecular manganese fluorides either from the reaction between  $\text{MnF}_3$  and  $\text{TbF}_4$ <sup>23</sup> or by thermal evaporation of Mn atoms in the presence of fluorine.<sup>11</sup>

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