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Published in:
Journal of Physical Chemistry C

DOI:
10.1021/acs.jpcc.3c02059

Published: 29/06/2023

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A Fresh Look at a Well-Known Solid: Structure, Vibrational Spectra, and Formation Energy of NaNH₂

Published as part of The Journal of Physical Chemistry virtual special issue “Early-Career and Emerging Researchers in Physical Chemistry Volume 2”.

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Cite This: J. Phys. Chem. C 2023, 127, 12287−12294

ABSTRACT: Sodium amide (NaNH₂) in its α form is a common compound that has recently seen renewed interest, mainly for its potential use as a solid-state hydrogen storage material. In this work, we present a synergic theoretical and experimental characterization of the compound, including novel measured and simulated vibrational spectra (IR and Raman) and X-ray diffraction patterns. We put forward the hypothesis of a low-temperature symmetry breaking of the structure to space group $C\bar{2}/c$, while space group $Fddd$ is commonly reported in the literature and experimentally found down to 80 K. Additionally, we report a theoretical estimate of the heat of formation of sodium amide from ammonia to be equal to $-12.2$ kcal/mol at ambient conditions.

INTRODUCTION

Solutions of alkali and alkaline earth metals in liquid ammonia have drawn the attention of the scientific community since the beginning of the last century for their use in strictly chemical or electrochemical processes.\(^{1-6}\) The typical reaction that takes place leads to the formation of amides $\text{MNH}_2$ ($\text{M} =$ alkali metal), and they can be schematized as

$$\text{M}(s) + \text{NH}_3(l) \rightarrow \text{MNH}_2(s) + \frac{1}{2}\text{H}_2(g) \quad (1)$$

This reaction has been characterized from different points of view, from kinetics\(^7\) to the equilibrium constant,\(^8\) from the catalysis\(^9\) to electrical conductivity,\(^1\) and so forth. NaNH₂ can also act as an intermediate in the decomposition of ammonia to nitrogen and hydrogen.\(^10\)

Recently, amides of alkali metals together with lightweight metal hydrides have drawn attention as solid-state hydrogen storage materials.\(^11-17\) The most extensively studied one is probably lithium amide (LiNH₂), which is characterized by great storage capacities (8.7 wt % of hydrogen content).\(^15-17\)

Among these materials, NaNH₂ is of considerable interest because of its role in the dehydrogenation of other light metal hydride systems, by forming composite hydrogen storage materials, as in NaNH₂−LiBH₄ and others.\(^18-21\) Moreover, sodium is not such a critical raw material as lithium.

Sodium amide has been characterized from different points of view: structural and electronic properties\(^22-27\) have been investigated together with vibrational properties,\(^23,26,29\) both at ambient conditions and at high pressures. Nonetheless, the number of theoretical studies of solid NaNH₂ seems not to be very large to date.\(^23,25,30\)

In this paper we intend to partly fill this gap, by (i) studying its structural stability and actually unveiling a possible low-temperature symmetry breaking; (ii) simulating IR and Raman spectra, with subsequent vibrational modes assignment; and (iii) simulating powder XRD patterns. All computed properties are complemented by and compared with new, original experimental data. Furthermore, we also evaluate computationally the heat of reaction of eq 1 at ambient conditions and at the athermal limit.

The paper is organized as follows: in the next section, experimental and computational details are reported, followed by the results of our work, unveiling a symmetry breaking from the $Fddd$ to a $C\bar{2}/c$ structure; powder X-ray diffraction patterns, heat of reaction calculations, as well as vibrational spectra (IR and Raman) are discussed; in the last section, final conclusions of our work are summarized.
Methods

Computational Details. We used a development version of the CRYSTAL23 code for all the calculations, which adopts atom-centered Gaussian-type functions, along with a PBE0 hybrid exchange-correlation functional. van der Waals dispersion interactions were accounted for through the empirical DFT-D4 method, which improves upon the D3 dispersion correction scheme especially for ionic systems. The adopted basis sets are pob-TZVP-rev2 for N and H and pob-TZVP for Na. The integration over the Brillouin zone in the reciprocal space was performed using a $8 \times 8 \times 8$ Monkhorst-Pack grid for NaNH$_2$, a $12 \times 12 \times 12$ grid for Na, considering a $2 \times 2 \times 2$ supercell, and a $6 \times 6 \times 6$ grid for NH$_3$. The thresholds that control the five truncation criteria ($T_i$) of the Coulomb and exchange infinite lattice series have been set to $7 (T_1-T_4)$ and $25 (T_5)$. The threshold for convergence on total energy has been set to 10.

The vibrational mode frequencies are evaluated according to the harmonic approximation, the Hessian is evaluated as the numerical derivative of first-order analytical gradients, and intensities are computed through a coupled-perturbed scheme.

Experimental Details. From the experimental side, all work was carried out trying to exclude moisture and air in an atmosphere of dried and purified argon ($5.0$, Praxair) using high-vacuum glass lines and a glovebox (MBraun). Liquid ammonia was dried by storage under fine vacuum several times before utilization.

Synthesis. Na (Acros, >99.5%) was freed from any crusts under hexanes and placed into a flame-dried Schlenk vessel under Ar. After pumping off any residual hexanes, the Na was molten in vacuum using a Bunsen burner and slowly poured into an attached glass ampule and flame-sealed. Any hydroxides or oxides present stuck to the glass surface of the Schlenk vessel, and pure Na flowed into the ampule. A flame-dried borosilicate glass ampule with $8 \text{mm}$ inner diameter was charged in the glovebox with Na metal (12 mg, 0.5 mmol); the ampule was closed using a glass valve, taken out of the glovebox, and attached to a Schlenk line for the work with anhydrous NH$_3$. In an Ar counter stream, a trace amount of rust was added to catalyze the reaction. The ampule was evacuated and cooled to $-78 \degree C$ using dry ice/isopropanol; ca. 2 mL of NH$_3$ was distilled into it, and the Na dissolved first with bronze and then with blue color. The ampule was then cooled to liquid N$_2$ temperature and flame-sealed under vacuum. The sealed-off tube was stored for 6 h at room temperature during which the solution became colorless and colorless NaNH$_2$ precipitated in quantitative yield. To grow crystals large enough for the diffraction experiment, the flame-sealed ampule was placed into a heating block at $40 \degree C$ for 5 days. The ampule was cooled to liquid nitrogen temperature and cut open under Ar, and the residual NH$_3$ evaporated at room temperature and then under vacuum. NaNH$_2$ was obtained as a white powder in quantitative yield.

Powder X-ray Diffraction. The sample was filled into a predried borosilicate glass capillary with a diameter of 0.3 mm. The powder X-ray pattern was recorded with a StadiMP diffractometer (Stoe & Cie) in the Debye–Scherrer geometry. The diffractometer was operated with Cu–K$_\alpha$1 radiation (1.5406 Å, germanium monochromator) and equipped with a MYTHEN 1K detector. The diffraction pattern was indexed using the WinXPOW suite.

Results and Discussion

Structure and Stability. Hypothesis for a Symmetry Breaking in the NaNH$_2$ Structure. Literature reports that the thermodynamically most stable polymorph of NaNH$_2$ at ambient conditions is the orthorhombic $\alpha$ structure (space group Fd$\bar{d}$, 70). After a first geometry optimization in that symmetry, however, we found one imaginary frequency (about 112 i cm$^{-1}$, B$_{2g}$ symmetry), indicating this structure is not a true local minimum.

We show in Figure 1 the computed potential energy surface along this normal mode, which actually shows that a lower-energy structure follows from symmetry breaking—the
corresponding subgroup is monoclinic, \( C_2/c \). In Figure 1, the red dots are the results of our calculations, while the blue curve is the result of cubic spline interpolation of our data.

We reoptimized the structure from the observed minimum, and detailed information is found in Table 1.

Such symmetry breaking is not uncommon and is similar to what we recently observed in a different system, namely \( \text{Li}_2\text{PS}_3\text{Cl} \). Clearly, the energy barrier between the optimized structures in \( \text{Fddd} \) and \( C_2/c \) space groups is very small (only about 0.02 eV), and thus, already at this stage, we do not expect such symmetry breaking to be measurable at room temperature conditions.

Figure 2 shows that the structural difference between the optimized geometries is not very large, the most notable features being a slight change in the alpha angle, a variation in the \( a \) and \( b \) lattice parameters, and a change in Na–N distances.

As expected, the change in the computed electronic structure is also not too relevant: the band gap is 4.29 eV for \( \text{NaNH}_2 \) in space group \( C_2/c \) and 4.27 eV in space group \( \text{Fddd} \). Such values—computed with hybrid functionals—are larger than those obtained from LDA calculations in previous works.

Compared with the experiments, our optimized cell is about 6% smaller in volume. Considering that our calculations are carried out at the athermal limit and the delicate balance of the whole computational setup, we deem such a result more than satisfactory.

**X-ray Diffraction Pattern.** In order to investigate further the \( \text{Fddd} \) vs \( C_2/c \) puzzle of solid \( \text{NaNH}_2 \), we carried out single crystal X-ray diffraction at 80 K of sodium amide single crystals. A splitting of the reflections at high angles would potentially indicate a lowering to monoclinic symmetry. The structure resulted, however, to be still orthorhombic \( \text{Fddd} \), and no splitting of reflections was observed. Considering the low energy difference between the two structures and that all atoms show very strong thermal vibrations,\(^{22}\) it is likely that the phase transition occurs at lower temperatures. For this reason, additional investigations could be performed, such as a measurement of heat capacitities down to 2 K and neutron diffraction patterns, which we leave for future work.

We computed the powder X-ray diffraction (PXRD) pattern for \( \text{NaNH}_2 \) in both \( \text{Fddd} \) and \( C_2/c \) space groups, considering an incident wavelength equal to 1.5406 Å, correspondent to the \( \text{Cu-K} \alpha \) line. In Table 2 and Figure 3 we compare such a computed pattern with our experimental one and experimental data from the literature.\(^{24}\)

<table>
<thead>
<tr>
<th>hkl</th>
<th>exp. (^{24})</th>
<th>exp.</th>
<th>calc. ( \text{Fddd} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>17</td>
<td>17.047</td>
<td>17.44 (+2.3%)</td>
</tr>
<tr>
<td>220</td>
<td>26</td>
<td>26.194</td>
<td>26.50 (+1.2%)</td>
</tr>
<tr>
<td>022</td>
<td>27</td>
<td>27.929</td>
<td>28.97 (+3.7%)</td>
</tr>
<tr>
<td>131</td>
<td>29</td>
<td>29.631</td>
<td>30.52 (+3.0%)</td>
</tr>
<tr>
<td>311</td>
<td>33</td>
<td>33.121</td>
<td>33.23 (+0.3%)</td>
</tr>
<tr>
<td>113</td>
<td>36</td>
<td>35.908</td>
<td>37.22 (+3.7%)</td>
</tr>
<tr>
<td>400</td>
<td>40</td>
<td>40.279</td>
<td>40.10 (+0.4%)</td>
</tr>
<tr>
<td>331</td>
<td>41</td>
<td>41.351</td>
<td>41.93 (+1.4%)</td>
</tr>
<tr>
<td>133</td>
<td>43.5</td>
<td>43.687</td>
<td>45.27 (+3.6%)</td>
</tr>
<tr>
<td>004</td>
<td>45</td>
<td>44.944</td>
<td>46.79 (+4.1%)</td>
</tr>
<tr>
<td>422</td>
<td>49</td>
<td>49.727</td>
<td>50.22 (+1.0%)</td>
</tr>
<tr>
<td>224</td>
<td>53</td>
<td>52.802</td>
<td>54.58 (+3.4%)</td>
</tr>
<tr>
<td>153</td>
<td>57</td>
<td>56.636</td>
<td>58.75 (+3.7%)</td>
</tr>
<tr>
<td>260</td>
<td>57</td>
<td>56.636</td>
<td>58.35 (+3.0%)</td>
</tr>
<tr>
<td>404</td>
<td>62</td>
<td>61.920</td>
<td>63.28 (+2.2%)</td>
</tr>
</tbody>
</table>

\(^{24}\)Experimental results are obtained at room temperature, while the calculated ones are referred to the optimized structure at the athermal limit. In parentheses, the deviations of calculated values from observed ones are given.
of the basis set for the treatment of metallic systems is crucial, and very diffuse functions are needed to correctly reproduce the density characterizing them. However, in order to obtain comparable results with the other studied compounds, a coherent level of theory was necessary, leading to the choice of the pob-TZVP basis set for Na, which Peintinger et al. indicated as suitable for the study of metallic sodium too, without the addition of diffuse valence functions.

We computed the heat of the reaction as

$$\Delta H^0 = \sum_p \nu_p \Delta H_p - \sum_r \nu_r \Delta H_r$$

(2)

where $p$ is the index for the products and $r$ is the index for the reagents.

The thermodynamic function for ambient conditions was obtained from the frequency calculations (using a $2 \times 2 \times 2$ supercell in the case of metallic Na). Results are reported for all the species involved in the reaction in Table 3.

Table 3. Thermodynamic Functions (a.u./cell for Solids and a.u. for H$_2$) at 298.15 K and 0.101325 MPa of the Na 2 × 2 × 2 Supercell, NH$_3$, Fddd– and C2/c–NaNH$_2$, and H$_2$

<table>
<thead>
<tr>
<th></th>
<th>EL</th>
<th>E0</th>
<th>ET</th>
<th>PV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na supercell</td>
<td>−1297.667964</td>
<td>0.005261</td>
<td>0.015110</td>
<td>0.000006</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>−226.081078</td>
<td>0.152115</td>
<td>0.008553</td>
<td>0.000003</td>
</tr>
<tr>
<td>H$_2$</td>
<td>−1.166063</td>
<td>0.010125</td>
<td>0.002360</td>
<td>0.000944</td>
</tr>
<tr>
<td>Fddd–NaNH$_2$</td>
<td>−872.629640</td>
<td>0.098224</td>
<td>0.014555</td>
<td>0.000004</td>
</tr>
<tr>
<td>C2/c–NaNH$_2$</td>
<td>−872.630207</td>
<td>0.099387</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(298.15 K)</td>
<td>−1297.647586</td>
<td>−1297.662702</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na supercell</td>
<td>−225.920407</td>
<td>−225.928963</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>−1.155363</td>
<td>−1155938</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fddd–NaNH$_2$</td>
<td>−872.516857</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2/c–NaNH$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

"EL = electronic energy, E0 = zero-point energy, ET = thermal contribution to the vibrational energy, PV = pressure by volume, H(298.15 K) = EL + E0 + ET + PV; H(0 K) = EL + E0. For C2/c–NaNH$_2$ just EL, E0, and H at the athermal limit are reported; for Fddd–NaNH$_2$ EL, E0, ET, PV, and H at 298.15 K are reported.

Our estimate for the heat of reaction at 298.15 K is −12.2 kcal/mol (−51.1 1 kj/mol) for NaNH$_2$ in space group Fddd, since it is the stable polymorph at ambient conditions, which is in very good agreement with previously reported experimental values of −12.3 and −11.7 kcal/mol. At the athermal limit, our $\Delta H^0$ estimate is −12.9 kcal/mol (−54.1 1 kJ/mol) for NaNH$_2$ in space group C2/c, since it is supposed to be the equilibrium structure at low temperature. By increasing the supercell size, such results change only marginally (0.35 kcal/mol).

Vibrational Spectra. Infrared Spectrum. We simulated the IR spectrum of NaNH$_2$ in both Fddd and C2/c space groups, which we report in Figure 4 and Table 4. The experimental IR spectrum was recorded at ambient temperature, while simulated IR is at the athermal limit. At a first glance it is evident that the computed spectra are both in general agreement with our experimental one which, in turn, is fully coherent with the available literature data. The most notable discrepancy is found in the range 800–1500 cm$^{-1}$ where some unpredicted features appear in the experimental spectrum. These peaks are not visible even in other experimental IR spectra reported in the literature, and we
were not able to identify their origin. Overall, the simulated IR spectra for the orthorhombic and monoclinic structures do not show significant differences. Let us look more in detail at the specific frequency ranges.

The band reported at the 609 cm$^{-1}$ wavenumber in the work of Liu and Song$^{28}$ and corresponding to the 591 cm$^{-1}$ wavenumber in our experimental spectrum is a very broad one, and it may be related to the convolution of three or more bands since the shape is not as well-defined as the other ones. In all our simulations, we notice a rigid shift in the group of frequencies, as a direct consequence of the underestimation of the cell volume reported in the previous section and harmonic approximation, reflected on these collective vibrational modes.

In the IR spectrum simulated for the structure with $C_{2}/c$ symmetry, the appearance of three bands can be observed, while the $F_{ddd}$ spectrum reports in this region an intense band at 634 cm$^{-1}$ and a weak one at 580 cm$^{-1}$. However, even if the broadening of the experimental band can be related to the convolution of more bands, its origin could possibly be of a different nature.

In the other regions we see no decisive feature in the spectra for the different structures, all in good agreement with the experiment. An extra band with weak intensity is estimated to be around 1590 cm$^{-1}$ in the simulated spectrum for the $C_{2}/c$ space group, and it is related to bending of the N–H bond. After the usual rescaling of the frequencies due to anharmonicity (we adopted here a factor of 0.95), also the high-frequency H-stretching modes compare well.

**Raman Spectrum.** We computed powder (direction-averaged) Raman spectra for the different structures of NaNH$_2$, using the same algorithm as described above for band positions and analytical evaluation of intensities.$^{52}$ We took also into account the experimental conditions (temperature and laser wavelength) to calculate Raman intensities. The experimental Raman spectrum was measured using three different lasers working at 488, 532, and 633 nm. For comparison with the calculated data, we considered the 488 nm one.

In Figure 5, a comparison among calculated and experimental spectra is presented, while in Table 5 the frequencies of the most intense bands are reported for a comparison among data from the literature, our experimental results, and calculated ones. The experimental Raman spectrum was recorded at room temperature, and the simulated spectrum was obtained by setting the temperature equal to 298 K and the incoming laser wavelength equal to 488 nm.

In the low-frequency region of the Raman spectrum, the number of bands in the calculated spectra is higher than that of the experimental one. It is worth remembering here that the computed intensity is interpreted as the band height, and a uniform broadening is applied, while this quantity is more properly to be interpreted as the band area. It is clear here that the experimental bands—especially those in the 400–600 cm$^{-1}$ region—all have different broadening, much larger than the reported ones, and hence they may largely overlap with each other. For instance, the experimental bands at 470 and 533 cm$^{-1}$ may well be the convolution of two of the four bands which are individuated in the calculated spectra for $F_{ddd}$ and

![Figure 4](image-url)

Figure 4. On the left, experimental (room temperature) and calculated (athermal limit) IR spectra comparison of NaNH$_2$ for the different optimized geometries; on the right, zoomed-in IR spectra zones (in order from top to bottom: 500–800, 1350–1700, and 3100–3300 cm$^{-1}$ (scaled by a factor of 0.95)). The calculated spectra are convoluted with a full width at half-maximum of 8 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Experimental</th>
<th>calc. $F_{ddd}$</th>
<th>calc. $C_{2}/c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>609</td>
<td>591</td>
<td>634</td>
<td>653</td>
</tr>
<tr>
<td>1530</td>
<td>1528</td>
<td>1528</td>
<td>1529</td>
</tr>
<tr>
<td>3212</td>
<td>3208</td>
<td>3368 (3200)</td>
<td>3366 (3198)</td>
</tr>
<tr>
<td>3259</td>
<td>3257</td>
<td>3442 (3270)</td>
<td>3441 (3269)</td>
</tr>
</tbody>
</table>

*In parentheses, scaled values of frequencies (scale factor = 0.95) can be found.*

Table 4. Experimental (Room Temperature) and Calculated (Athermal Limit) IR Frequencies (cm$^{-1}$) Comparison of NaNH$_2$ for the Different Geometries$^{46}$

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**Raman Spectrum.** We computed powder (direction-averaged) Raman spectra for the different structures of NaNH$_2$, using the same algorithm as described above for band positions and analytical evaluation of intensities.$^{52}$ We took also into account the experimental conditions (temperature and laser wavelength) to calculate Raman intensities. The experimental Raman spectrum was measured using three different lasers working at 488, 532, and 633 nm. For comparison with the calculated data, we considered the 488 nm one.

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<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Experimental</th>
<th>calc. $F_{ddd}$</th>
<th>calc. $C_{2}/c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>609</td>
<td>591</td>
<td>634</td>
<td>653</td>
</tr>
<tr>
<td>1530</td>
<td>1528</td>
<td>1528</td>
<td>1529</td>
</tr>
<tr>
<td>3212</td>
<td>3208</td>
<td>3368 (3200)</td>
<td>3366 (3198)</td>
</tr>
<tr>
<td>3259</td>
<td>3257</td>
<td>3442 (3270)</td>
<td>3441 (3269)</td>
</tr>
</tbody>
</table>

*In parentheses, scaled values of frequencies (scale factor = 0.95) can be found.*
C2/c structures, which are reported in Table 5. The same can be observed for experimental bands at 177, 247, and 380 cm\(^{-1}\).

A blue shift of bands can be noticed as observed in the IR, but no crucial differences can be individuated between the simulated Raman spectra of orthorhombic and monoclinic structures.

In the region around 1500 cm\(^{-1}\), only one band appears, corresponding to the symmetric bending of the N–H bond. It is possible to find a better agreement between the experimental frequency and the calculated one for the Fddd structure, as expected since the orthorhombic polymorph is the most stable one at room temperature. However, an extra shoulder band appears in the Fddd system.

The calculated frequencies of the bands in the high-wavenumber region have been once more downscaled to empirically account for missed anharmonic effects (scale factor = 0.95). However, we found no valuable information in the analysis of these particular bands.

Furthermore, we calculated the anisotropic displacement parameters (ADPs) for all the structures. ADP is a 3×3 tensor associated with each atom of the unit cell. Diagonalizing the resulting tensors, we obtained three positive eigenvalues for each irreducible atom of the cell which define the length of the principal axes of the ellipsoids. The ellipsoids define the surfaces of constant probability of atomic displacement. In Figures 6 and 7 we show the calculated ADPs for structures in the Fddd and C2/c space groups, respectively. As can be seen, the ADPs of all atoms, especially for hydrogens, of the structure in the Fddd space group are larger than those of the monoclinic structure. This observation seems to be in agreement with that reported by Nagib et al.\(^{22}\) We observed the same behavior by considering NaNH\(_2\) in both Fddd and

---

**Table 5. Experimental (Room Temperature) and Calculated (298 K) Raman Frequencies (cm\(^{-1}\)) Comparison of NaNH\(_2\) for the Different Geometries**

<table>
<thead>
<tr>
<th></th>
<th>exp.(^{20})</th>
<th>exp.(^{55})</th>
<th>exp.</th>
<th>calc. Fddd</th>
<th>calc. C2/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>62</td>
<td>89</td>
<td>81</td>
<td>108</td>
<td>200</td>
</tr>
<tr>
<td>177</td>
<td>177</td>
<td>172</td>
<td>152</td>
<td>185</td>
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\(^{a}\)In parentheses, scaled values of frequencies (scale factor = 0.95) can be found.

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The calculated frequencies of the bands in the high-wavenumber region have been once more downscaled to empirically account for missed anharmonic effects (scale factor = 0.95). However, we found no valuable information in the analysis of these particular bands.

**Figure 5.** On the left, room temperature experimental and calculated Raman spectra comparison of NaNH\(_2\) for the different optimized geometries; on the right, zoomed-in Raman spectra zones (in order from top to bottom: 50–800, 1300–1700, and 3100–3350 cm\(^{-1}\)) (scaled by a factor of 0.95). The calculated spectra are convoluted with a full width at half-maximum of 8 cm\(^{-1}\).

**Figure 6.** Fddd-NaNH\(_2\) anisotropic displacement ellipsoids. Color code: Na yellow, N blue, and H pink.
C2/c space groups. This observation supports our hypothesis of a symmetry breaking and suggests that hydrogen atoms are responsible for it. In fact, since XRD cannot localize them perfectly and in the Fddd-type structure they strongly waggle, it is reasonable to expect a lowering of symmetry. Neutron diffraction on NaNH$_2$ should be performed to verify our hypothesis.

**CONCLUSIONS**

In this work, we present a synergic computational and experimental study of NaNH$_2$. All calculations are ab initio and carried out at the athermal limit. In Raman spectra, which are evaluated within the Placzek approximation,$^{14}$ room temperature and laser wavelength are approximately taken into account as a simple prefactor to peak intensities. From vibrational calculations, we found its Fddd structure to be metastable. A lower-energy structure was identified characterized by C2/c symmetry. However, from acquired X-ray diffraction data on single crystals of sodium amide at 80 K, the crystal structure resulted to be still orthorhombic rather than monoclinic. Further analysis should be performed in order to verify if a phase transition occurs at lower temperature. However, analysis of anisotropic displacement parameters of sodium amide atoms in both Fddd and C2/c space groups supports our hypothesis of a lowering of symmetry because of the very large displacements of H (and D) atoms in the Fddd-type structure.

Finally, due to the role of sodium amide in hydrogen storage applications, we also calculated the NaNH$_2$ formation reaction enthalpy from Na and NH$_3$, which leads to the evolution of H$_2$. The resulting values at ambient conditions are equal to $-12.2$ kcal/mol for the orthorhombic system, which is in very good agreement with experimental results ($-12.3$ kcal/mol).$^{50}$

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c02059.

Supplementary material, including (i) additional details on the optimized NaNH$_2$ structures and standardization of monoclinic crystal structure; (ii) analysis of XRD patterns for the monoclinic system, structure factors for both Fddd- and C2/c-NaNH$_2$ and simulated PXRD pattern considering experimental lattice parameters; and (iii) larger IR and Raman spectra of the two structures (PDF).

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Funding from the Erasmus+ Cooperation Partnerships programme—VISUENERGY project (2021-1-FI01-KA220-HED-000023408)—is gratefully acknowledged. Authors acknowledge support from the Project CH4.0 under the MUR program “Dipartimenti di Eccellenza 2023-2027” (CUP: D13C22003520001).

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