# NMR Chemical Shifts in Hard Carbon Nitride Compounds

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We show that NMR chemical shift spectroscopy could help to identify the crystalline phases of hard carbon nitride compounds. To this purpose we compute the NMR chemical shifts of defect zinc-blende, cubic, $\alpha-$, $\beta-$, and graphitic $C_3N_4$ with a newly developed *ab initio* method. The C shifts can be used to identify the CN bonds and to characterize C hybridization. The N shifts distinguish the $\alpha$-$C_3N_4$ from the $\beta$-$C_3N_4$ phases, and indicate the presence of the graphitic phase. [S0031-9007(98)05665-8]

Carbon nitride compounds have been predicted [1] to exhibit extraordinary hardness, with some structures possibly being harder than diamond [2]. This has stimulated substantial research efforts in search of these materials, employing both experimental [3–14] and theoretical [2,13,15,16] methods.

Shortly after the possibility of high bulk modulus due to the expected short C-N bond lengths was recognized [1], the $\beta$-$C_3N_4$ [2] and later the defect zinc-blende [16], $\alpha$-$C_3N_4$ [2], and cubic-$C_3N_4$ [2] structures were proposed. The theoretical bulk moduli of these structures are 427, 425, 425, and 496 GPa, respectively. Experimental studies, mostly on thin films, followed soon, finding nanometer to micrometer sized crystals embedded usually in an amorphous matrix [3,6,8,11,12]. In several cases [3,6,11] the crystallites were believed to be of the $\beta$-$C_3N_4$ structure, but it has been pointed out later [2] that the $\alpha$-$C_3N_4$ structure would comply better with the experimental data. Crystallites with a tetragonal structure [12] and even a monoclinic phase [12] have been reported recently. When using a chemical precursor technique, the defect zinc-blende structure also appears to form [13].

In all experiments, the crystallites obtained are too small to allow a conclusive x-ray diffraction (XRD) analysis. Therefore, structural determinations have been done with XRD in combination with other techniques, e.g., electron diffraction [3,6,8,11–13], x-ray photoelectron spectroscopy [3,8,10], electron energy loss spectroscopy [4], backscattering [3,6,8,10,11,17], and transmission electron microscopy [6,11,12,14]. Still, the determination of the structure of the crystallites remains difficult and not definitive, often because of the obscuring signals from the amorphous matrix or the substrate [11].

In this Letter, we suggest the use of nuclear magnetic resonance (NMR) chemical shift for C-N compound sample characterizations. NMR shift experiments are becoming increasingly popular for characterizing thin-film samples of amorphous carbon [18–23] and silicon [24]. By applying a recently developed *ab initio* method [25], we predict the NMR chemical shifts for C and N atoms of five different low-energy $C_3N_4$ structures. Our theoretical

data allow an interpretation of experimental NMR spectra, thereby opening a new way for C-N compound characterization. Unlike XRD, NMR experiments do not require long range order, and, as we shall see, should be able to clearly identify the signals from the amorphous $sp^2$-bonded matrix, and the crystalline $sp^3$-bonded phases. Other phases, such as the defect zinc-blende and cubic $C_3N_4$ cannot be distinguished by their NMR chemical shift, and other experimental techniques must be invoked. To our knowledge, only two NMR shift experiments on thin amorphous $CN_x$ films have been performed [5,26], which showed the absence of $sp^3$ bonds, but did not aim at characterizing possible crystalline CN compounds.

Out of the many proposed structures, we pick the five different $C_3N_4$ candidates shown in Fig. 1 and compute their NMR chemical shifts [27]. The defect zinc-blende cubic structure [16] with space group $P\overline{4}3m$ is examined because of recent experimental findings [13]. We include the predicted low-compressibility cubic structure [2] with symmetry $I\overline{4}3d$, because of the potential technological importance of this hypothetical phase. Finally, we consider $\beta$-$C_3N_4$ [15] and $\alpha$-$C_3N_4$ [2] which have likely been observed in experiments. The aforementioned four structures all have C in $sp^3$ and N in a threefold coordination. That is, each C has four N neighbors and each N has three C neighbors. The fifth structure we study is the graphitic $C_3N_4$ phase [2], which is actually predicted to be the energetically most favorable form of $C_3N_4$. Here, the C atoms are all $sp^2$ bonded with three N neighbors. Two of the N atoms [1(a) and 1(f) in the Wyckoff site notations] are bonded to three C atoms; the others are in a twofold, bent coordination, with two C neighbors.

In NMR measurements, the chemical shift is one third of the trace of the chemical shift tensor, $\sigma(\mathbf{r}) = \text{Tr}[\overleftrightarrow{\sigma}(\mathbf{r})]/3$, which connects the induced magnetic field to the external uniform applied magnetic field, $\mathbf{B}_{in}(\mathbf{r}) = -\overleftrightarrow{\sigma}(\mathbf{r})\mathbf{B}_{ext}$. We compute $\sigma$ following Ref. [25]. The electronic structure is described using density functional theory in the local density approximation. As the core contributions to $\sigma$ for C and N are insensitive to the chemical environment [28], we consider the magnetic response
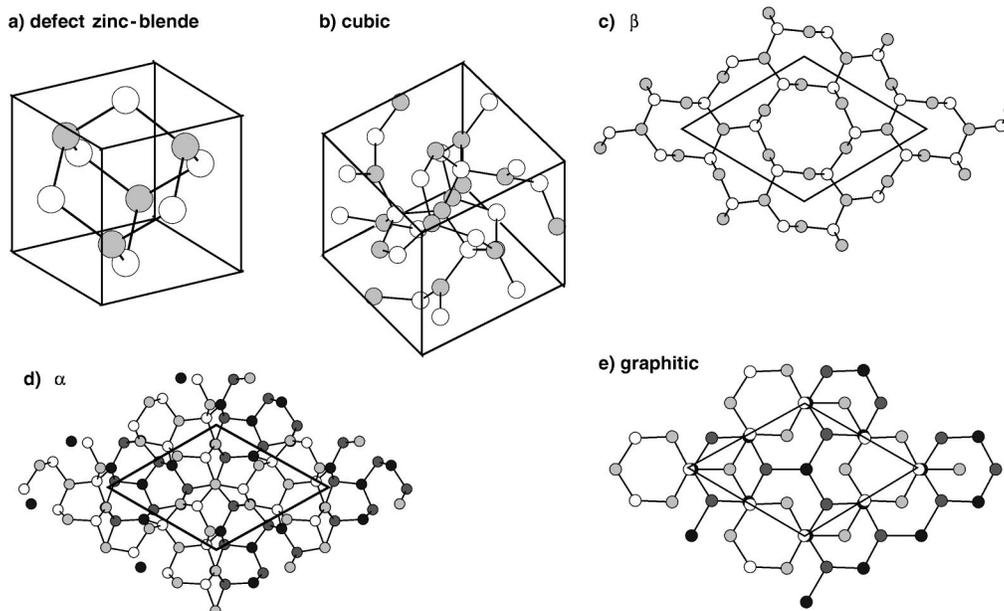
       

FIG. 1.   Ball and stick models of the studied $C_3N_4$ phases.  For the defect zinc-blende (a), cubic (b), and the $\beta$ phase (c); the C and N atoms are white and grey, respectively.  The $\alpha$ structure (d) and the graphitic phase (e) both consist of two layers.  The upper layer shows the C atoms in white and the N atoms in light grey.  In the lower layer, the C and N atoms are dark grey and black, respectively.

of the valence electrons only.  We use norm-conserving pseudopotentials [29] in the Kleinman-Bylander form [30].  For both C and N, nonlocal $s$ projectors augment the local potential.  We expand the wave functions in a plane-wave basis set up to an energy cutoff of 100 Ry [31].

Following the experimental convention, we will quote chemical shifts with respect to standard reference systems of a neat liquid sample with spherical shape at 300 K.  The C shifts are given with respect to tetramethyl-silane (TMS) [32] by $\delta_{TMS}(\text{sample}) = -[\sigma(\text{sample}) - \sigma(\text{TMS})]$, where $\sigma$ is the absolute chemical shift.  For N, nitromethane is used [32] as standard [33]: $\delta_{CH_3NO_2}(\text{sample}) = -[\sigma(\text{sample}) - \sigma(CH_3NO_2)]$.

To test the validity of our pseudopotential approach, and to explore trends in the C shifts, we calculate C $\delta$ for a set of small molecules (Table I).  In the series of molecules $CH_4$, $CH_3NH_2$, $CH_2(NH_2)_2$, $CH(NH_2)_3$, and $C(NH_2)_4$, the substitution of hydrogen by amine groups leads to deshielding of the C.  A similar effect, but less pronounced, is observed for N in the series $NH_3$, $CH_3NH_2$, $(CH_3)_2NH$, and $(CH_3)_3N$.  In all cases but pyridine, the neighbors of N are $sp^3$ C, i.e., all C-N bonds are single bonds like those in the hard CN compounds.  In these molecules, the agreement between computed and measured shifts is very good.  In pyridine $(NC_5H_5)$, since the C are $sp^2$ hybridized, the N $p_z$ orbital can form an additional resonant $\pi$ bond with the C $p_z$ orbitals like in the graphitic $C_3N_4$ phase.  The different bonding situation is reflected in much larger C and N $\delta$.  The theory reproduces the large increase of $\delta$, but the quantitative agreement with experiment is less satisfactory.

Table II shows the computed C chemical shifts for the five different $C_3N_4$ phases, along with the coordination number of the C atom.  The rightmost column gives the fraction of C atoms in this configuration, which relates to the relative intensity of the NMR signal.  Focusing on the shifts of the fourfold coordinated C atoms, we find they

TABLE I.   Computed and experimental C and N chemical shifts for selected molecules in the gas phase.  Values in parentheses are aligned with experiments [32,33].  Geometries are taken from Ref. [34] ($CH_4$), Ref. [35] ($CH_3NH_2$, $N_2H_4$), Ref. [36] ($NH_3$, pyridine, $(CH_3)_2NH$, $(CH_3)_3N$), and from relaxation within the local density approximation [$CH_2(NH_2)_2$, $CH(NH_2)_3$, $C(NH_2)_4$].

| Molecule | | C $\delta_{TMS}$ [ppm] Theory | Expt. | N $\delta_{CH_3NO_2}$ [ppm] Theory | Expt. |
|---|---|---|---|---|---|
| $CH_4$ | | $(-11)$ | $-11$[b] | | |
| $CH_3NH_2$ | | 27 | 26[b] | $-387$ | $-377$[a,c] |
| $CH_2(NH_2)_2$ | | 52 | | $-347$ | |
| $CH(NH_2)_3$ | | 67 | | $-332$ | |
| $C(NH_2)_4$ | | 80 | | $-321$ | |
| $(CH_3)_2NH$ | | 37 | | $-369$ | $-370$[a,c] |
| $(CH_3)_3N$ | | 45 | | $-362$ | $-363$[a,c] |
| $NH_3$ | | | | $(-402)$ | $-402$[d] |
| $N_2H_4$ | | | | $-340$ | $-335$[a,c] |
| Pyridine $(NC_5H_5)$ | $C_2$ | 132 | 150[a,e] | $-105$ | $-62$[a,f] |
| | $C_3$ | 108 | 124 | | |
| | $C_4$ | 117 | 136 | | |

[a]Experiments are done on liquid or solution.
[b]Ref. [38].
[c]Ref. [41].
[d]Ref. [39].
[e]Ref. [42].
[f]Ref. [34].

TABLE II. Computed C chemical shifts ($\delta_{TMS}$) and coordination number for five different $C_3N_4$ structures. The second column indicates the Wyckoff site of the atoms.

| $C_3N_4$ phase | Sites | C $\delta_{TMS}$ Theory [ppm] | Coord. | Fraction[a] |
|---|---|---|---|---|
| Defect zinc-blende[b] | 3(c) | 93 | 4 | 1 |
| Cubic[c] | 12(b) | 91 | 4 | 1 |
| $\beta$[b] | 6(h) | 82 | 4 | 1 |
| $\alpha$[c] | 6(c) | 86 | 4 | 1/2 |
|  | 6(c) | 86 | 4 | 1/2 |
| Graphitic[b] | 3(j) | 144 | 3 | 1/2 |
|  | 3(k) | 144 | 3 | 1/2 |

[a]Fraction of corresponding C atoms.
[b]Coordinates are taken from Ref. [16].
[c]Coordinates are from Ref. [2]; the two different 6(c) sites are labeled C(1) and C(2) in Ref. [2].

all fall within a fairly narrow range of about 80 to 90 ppm. This value is markedly different from fourfold coordinated diamond, which has a shift of 36 ppm (theory [23]) or 34.5 ppm (experiment [42]), but is close to the 80 ppm obtained for $C(NH_2)_4$ (Table I). A general trend can be observed for molecules with a tetrahedrally configured C atom, but varying ligands. For instance, in the series $CH_4$, $CCl_4$, and $CF_4$, the C $\delta_{TMS}$ is $-11.0$, 96.7, and 123.6 ppm, respectively, increasing with electronegativity [28].

Given the limited resolution of solid-state NMR experiments, it will be difficult to distinguish the first four phases from each other by looking at the C shifts alone. However, their signal appears between the $sp^3$ and $sp^2$ peaks of amorphous C [22] at about 70 and 130 ppm, respectively, and should be detectable if a sufficient fraction of the sample consists of such $C_3N_4$ compounds. For the graphitic $C_3N_4$ phase, we predict a carbon shift of 144 ppm. This larger shift is typical of $sp^2$ hybridized C.

In Table III we present the calculated N shifts of the $C_3N_4$ solids. Similar to the C shifts, we observe a large

TABLE III. Computed N chemical shifts ($\delta_{CH_3NO_2}$) and coordination number for five different $C_3N_4$ structures. The second column indicates the Wyckoff site of the atoms.

| $C_3N_4$ phase | Sites | N $\delta_{CH_3NO_2}$ Theory [ppm] | Coord. | Fraction[a] |
|---|---|---|---|---|
| Defect zinc-blende[b] | 4(e) | $-314$ | 3 | 1 |
| Cubic[c] | 16(c) | $-317$ | 3 | 1 |
| $\beta$[b] | 2(c) | $-314$ | 3 | 1/4 |
|  | 6(h) | $-311$ | 3 | 3/4 |
| $\alpha$[c] | 2(a) | $-335$ | 3 | 1/8 |
|  | 2(b) | $-258$ | 3 | 1/8 |
|  | 6(c) | $-307$ | 3 | 3/8 |
|  | 6(c) | $-313$ | 3 | 3/8 |
| Graphitic[c] | 1(a) | $-240$ | 3 | 1/8 |
|  | 1(f) | $-241$ | 3 | 1/8 |
|  | 3(k) | $-168$ | 2 | 3/8 |
|  | 3(j) | $-164$ | 2 | 3/8 |

[a]Fraction of corresponding N atoms.
[b]Coordinates are taken from Ref. [16].
[c]Coordinates are from Ref. [2]; the two different 6(c) sites are labeled N(3) and N(4) in Ref. [2].

difference between the graphitic phase and the other $C_3N_4$ structures. This is not unexpected, since the N at 3(k) and 3(j) positions of the graphitic phase are twofold coordinated unlike in any other compound, and all the N have their C nearest neighbors in $sp^2$ rather than $sp^3$ configuration. This allows resonant $\pi$ bonds between the N and its C neighbors. Equally important is the fact that the positions and the number of N peaks in $\alpha$-$C_3N_4$ are clearly different from those of the other $C_3N_4$ phases. This should allow one to resolve the question whether $\alpha$-$C_3N_4$ or $\beta$-$C_3N_4$ is observed in experiment [2]. However, neither the C nor the N shift is sufficient to distinguish the cubic and the defect zinc-blende $C_3N_4$.

The variation of the N shift in $\alpha$-$C_3N_4$ by about 75 ppm is surprising at first, since they are all threefold coordinated, and the bond lengths range only from 1.41 to 1.50 Å. Similarly, the calculated value for pyridine is $-105$ ppm (see Table I), which is 61 ppm shifted from the graphitic phase $-166$ ppm, although the coordination and geometry are comparable. Other researchers had noticed the extraordinary sensitivity of N shifts to their environment before. For example, in Ref. [28] the difference between the *cis* and *trans* isomers of an HNNH molecule is $\sim100$ ppm. This sensitivity has been attributed to the strong influence of the lone pair electrons [28]. In short, N shifts are difficult to determine from the geometry or from a comparison with molecular systems.

Notice that, in the experimental spectra on amorphous $CN_x$ [26], a peak at $-105$ ppm is found [43], which is not too far from the averaged $-166$ ppm shift we find for the twofold coordinated N in the graphitic $C_3N_4$ phase. However, the lack of a peak near $-240$ ppm from the threefold coordinated N indicates the absence of graphitic $C_3N_4$ in this experiment.

Finally, for completeness, we quote our calculated bulk magnetic susceptibilities (in $ppm\,cm^3/mol$) which are $-27$ (defect zinc-blende), $-29$ (cubic), $-37$ ($\alpha$-$C_3N_4$), $-34$ ($\beta$-$C_3N_4$), and $-37.5$ (graphitic $C_3N_4$).

In summary, our calculations demonstrate that NMR chemical shift experiments may be used to characterize the $C_3N_4$ compounds. The observed C shift should be clearly distinguishable from the amorphous C signal. The N shifts can be used to discern the $\alpha$- and $\beta$-$C_3N_4$ phases.

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[33] $\delta_{\text{CH}_3\text{NO}_2}$ for gas $\text{NH}_3$ is obtained as the sum of a shift of $-326.16$ ppm between the $\text{NH}_3$ and the $\text{N}_2$ isolated molecules [39], a $-74.7$ ppm shift between the isolated $\text{N}_2$ molecule and liquid $\text{CH}_3\text{NO}_2$ in a cylindrical sample perpendicular to the magnetic field [39], and finally a $-0.82$ ppm correction to a spherical sample shape.

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