Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

BEYOND MOLECULAR NITROGEN: TWO AMBIENT PRESSURE METASTABLE SINGLE- AND DOUBLE-BONDED NITROGEN ALLOTROPES BUILT FROM THREE-MEMBERED RINGS REVEALED

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Phys. Chem. Chem. Phys.

SUPPORTING INFORMATION

LIST OF SUPPLEMENTARY FIGURES AND TABLES:

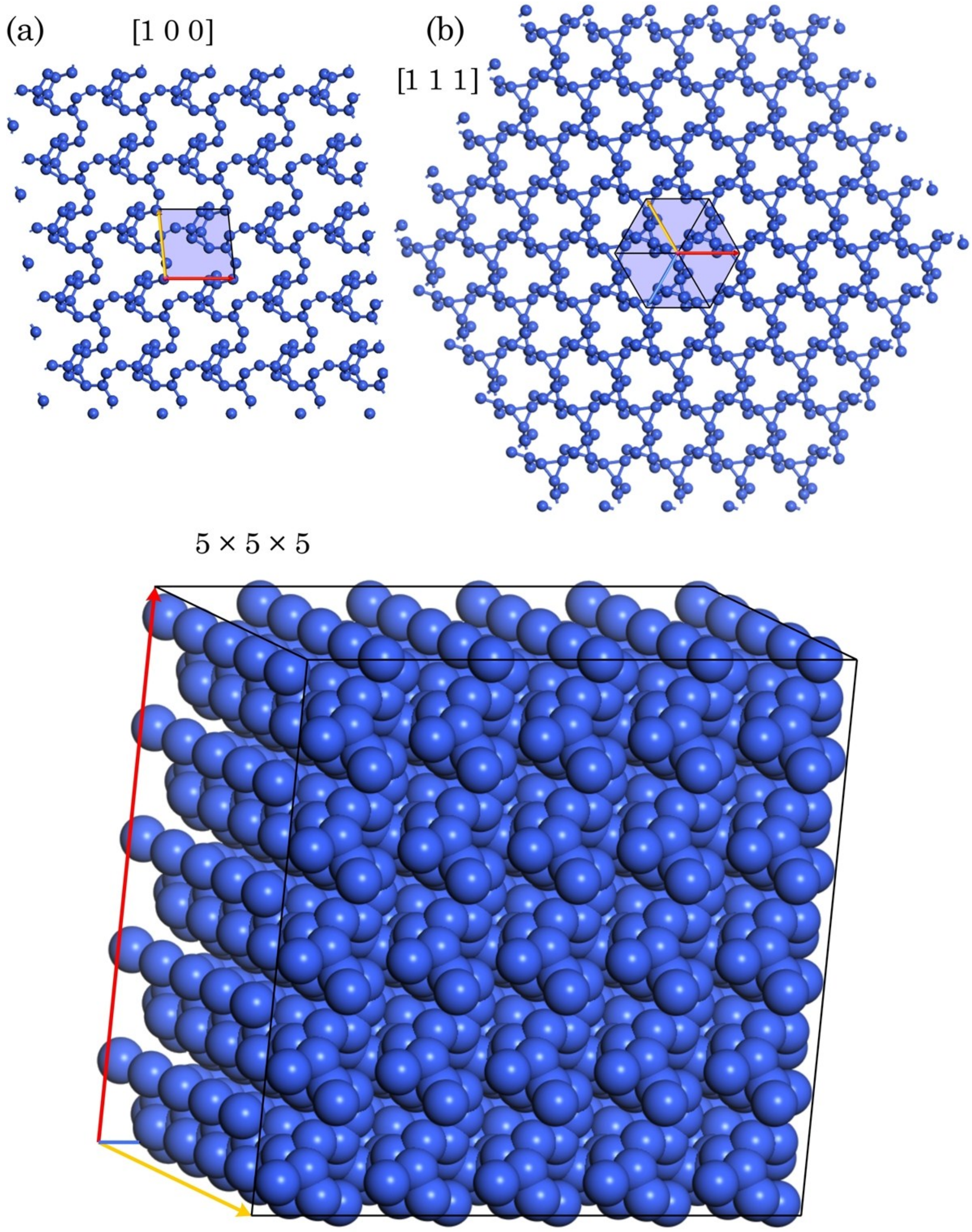


Fig. S1. Crystal packing of the DobN nitrogen allotrope.

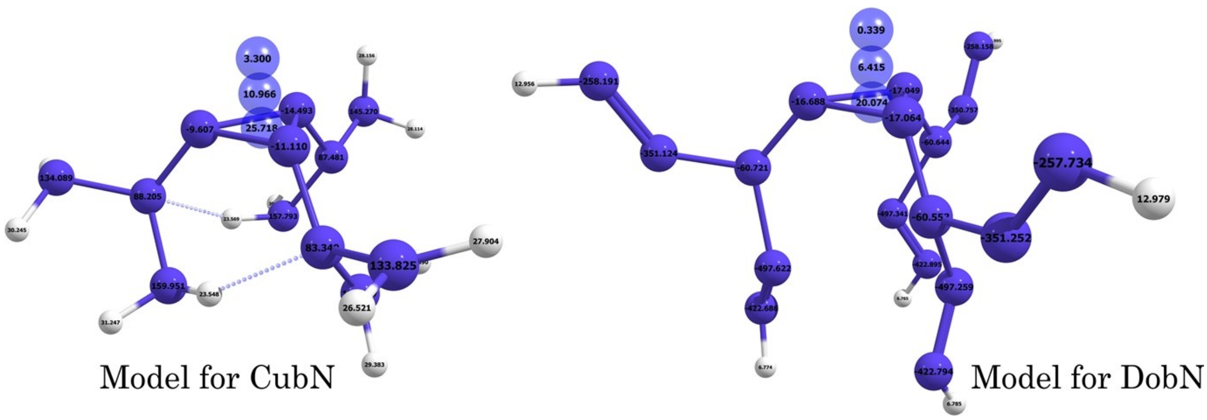


Fig. S2. The applied model structures for NICS calculations at the B3LYP/6-311+G(d,p) level of theory.

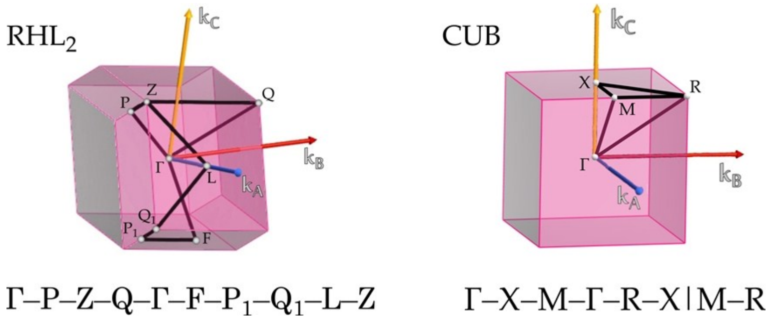
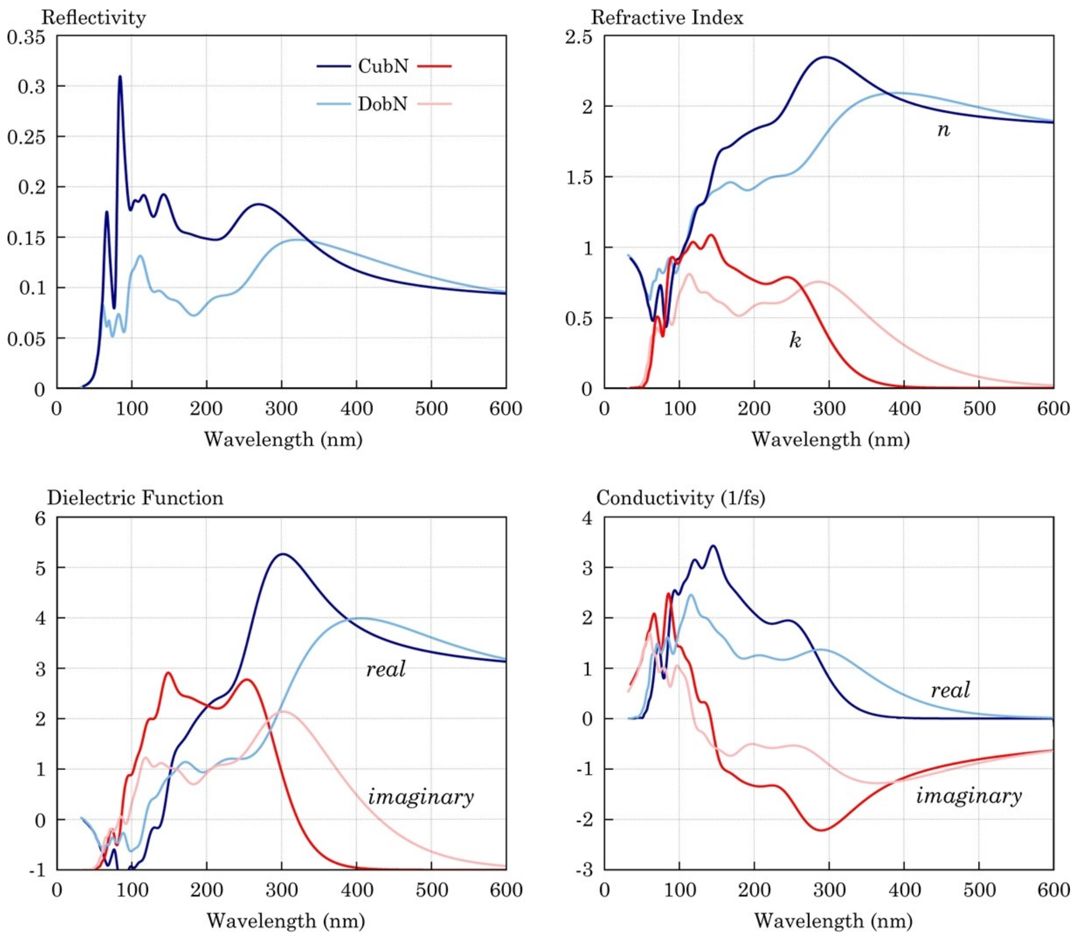
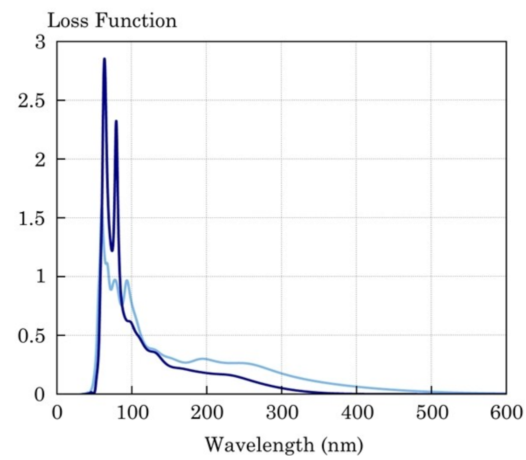


Fig. S3. The Brillouin zone integration paths within the high-throughput band structure calculations.





Reflectivity

$$R(\omega)=\left|\frac{\sqrt{\varepsilon(\omega)}-1}{\sqrt{\varepsilon(\omega)}+1}\right|^2 \qquad \text{(S1)}$$

Refractive Index

$$n(\omega)=\frac{\sqrt{2}}{2}\left[\sqrt{\varepsilon_1^2(\omega)+\varepsilon_2^2(\omega)}+\varepsilon_1(\omega)\right]^{1/2} \qquad \text{(S2)}$$

Conductivity

$$\sigma(\omega)=\sigma_1(\omega)+i\sigma_2(\omega)=-i\frac{\omega}{4\pi}\left(\varepsilon(\omega)-1\right) \qquad \text{(S3)}$$

Loss Function

$$\beta(\omega)=\mathrm{Im}\left(\frac{-1}{\varepsilon(\omega)}\right) \qquad \text{(S4)}$$

Fig. S4. The calculated optical properties of the CubN and DobN allotropes.

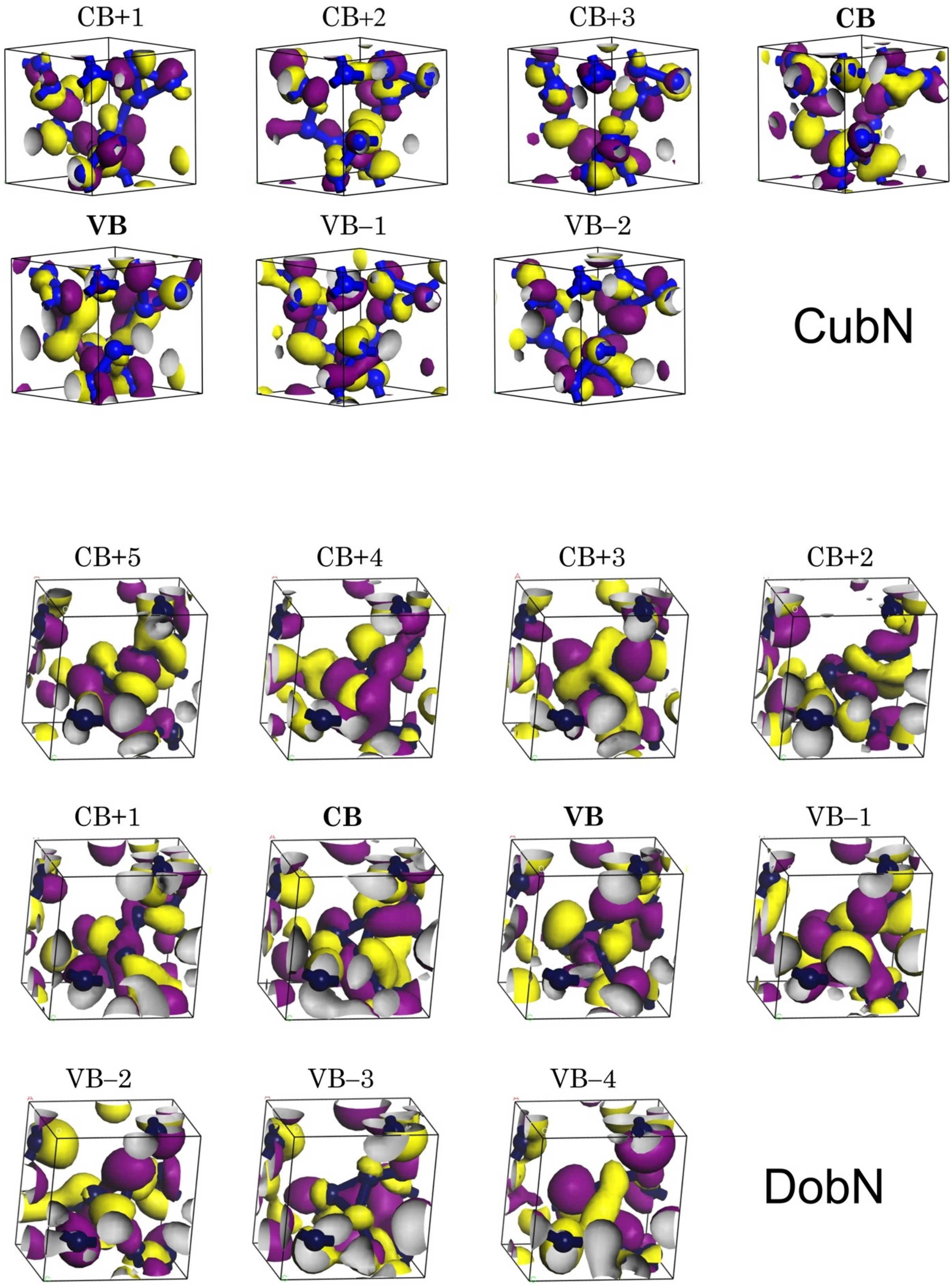


Fig. S5. The nature of electronic bands, which are involved in the first 12 electronic transitions of CubN and DobN.

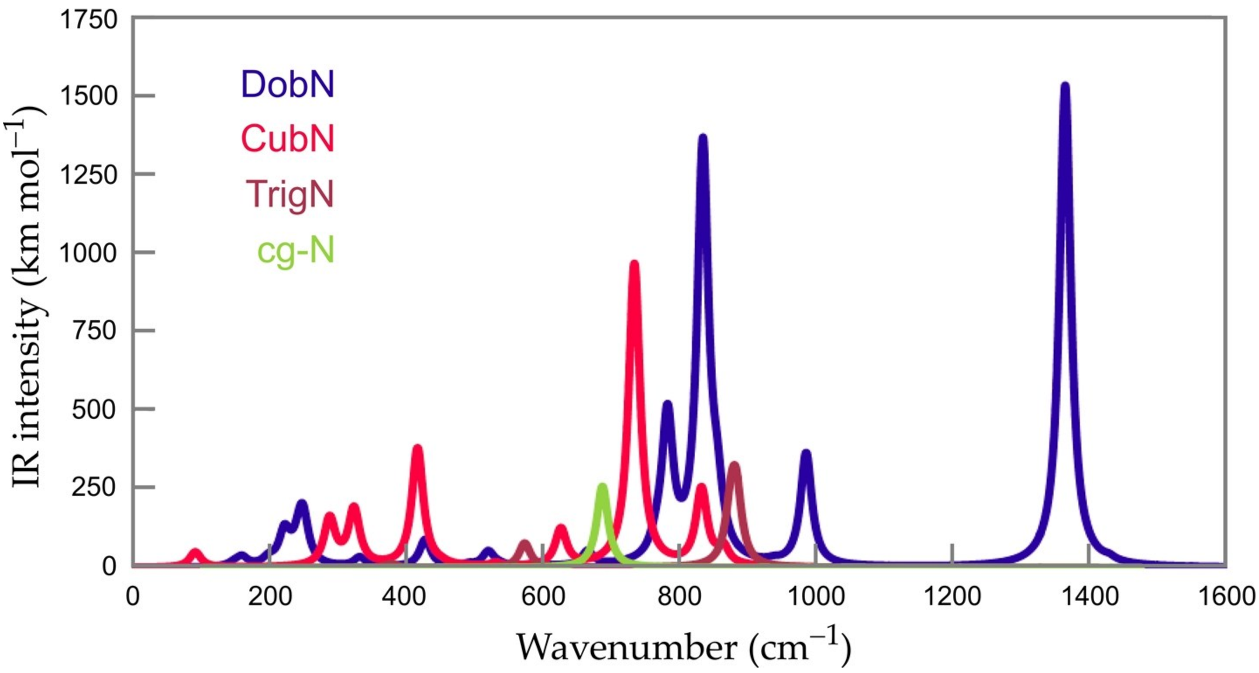


Fig. S6. The calculated IR spectra of several nitrogen allotropes.

Table S1. Numerical IR and Raman spectral data of the CubN and DobN allotropes

	CubN				DobN			
Mode	Symm.	ν (cm^{-1})	IR intensity $\left(\frac{D}{Å}\right)^2$ amu^{-1}	Raman intensity Å^4	Symm.	ν (cm^{-1})	IR intensity $\left(\frac{D}{Å}\right)^2$ amu^{-1}	Raman intensity Å^4
1	*b*	21.85		567.0088	*b*	148.59	0.2290	66.5660
2	*a*	99.51	0.3435	14.3009	*a*	159.94	0.3277	244.8286
3	*a*	99.51	0.3435	14.3009	*a*	159.94	0.3277	245.3315
4	*a*	99.51	0.3435	14.3009	*a*	198.74	0.2407	669.0525
5	*c*	170.98		72.1826	*a*	198.74	0.2407	669.0861
6	*c*	170.98		99.4036	*b*	222.26	2.4746	128.4505
7	*a*	288.23	1.1877	36.4249	*a*	242.17	0.4567	604.0838
8	*a*	288.23	1.1877	60.7469	*a*	242.17	0.4567	604.1904
9	*a*	288.23	1.1877	33.2708	*b*	248.59	3.8236	232.1349
10	*a*	323.79	1.4052	1171.8326	*a*	332.18	0.3470	1571.8549
11	*a*	323.79	1.4052	1171.9362	*a*	332.18	0.3470	1573.1543
12	*a*	323.79	1.4052	1163.9349	*b*	428.08	2.0469	687.7669
13	*c*	369.42		156.2332	*a*	491.98	0.0816	214.9953
14	*c*	369.42		177.2658	*a*	491.98	0.0816	215.6183
15	*a*	416.81	2.9618	270.4488	*a*	519.55	0.2581	203.7133
16	*a*	416.81	2.9618	270.4488	*a*	519.55	0.2581	204.0346
17	*a*	416.81	2.9618	270.4488	*b*	521.19	0.6272	1243.7423
18	*a*	450.98	0.0400	50.3312	*b*	536.80	0.1226	3284.3636
19	*a*	450.98	0.0400	39.5892	*a*	592.17	0.1511	267.9117
20	*a*	450.98	0.0400	87.8553	*a*	592.17	0.1511	268.3349
21	*b*	479.32		1115.2749	*b*	665.83	1.0627	906.3261
22	*a*	531.56	0.0850	149.3420	*b*	766.87	0.9995	15052.0833
23	*a*	531.56	0.0850	149.3420	*a*	782.80	5.3956	975.1451
24	*a*	531.56	0.0850	149.3420	*a*	782.80	5.3956	975.6277
25	*b*	537.89		1657.3019	*b*	834.62	31.0983	310.8172
26	*a*	626.72	0.9249	163.9845	*a*	855.46	1.8845	2574.2831
27	*a*	626.72	0.9249	163.9845	*a*	855.46	1.8845	2574.3534
28	*a*	626.72	0.9249	163.9845	*b*	938.29	0.1545	1993.8421
29	*c*	696.98		277.6668	*a*	985.81	4.2118	559.6803
30	*c*	696.98		294.0468	*a*	985.81	4.2118	560.4573
31	*a*	734.35	7.5689	2253.0295	*a*	1365.09	18.0682	369.2597
32	*a*	734.35	7.5689	2253.0295	*a*	1365.09	18.0682	369.3512
33	*a*	734.35	7.5689	2253.0295	*b*	1429.51	0.2284	1788.8490
34	*a*	832.59	1.9080	422.4139				
35	*a*	832.59	1.9080	419.6262				
36	*a*	832.59	1.9080	416.1194				
37	*a*	864.36	0.4289	13.9426				
38	*a*	864.36	0.4289	13.9426				
39	*a*	864.36	0.4289	13.9426				
40	*a*	897.32	0.0123	147.2006				
41	*a*	897.32	0.0123	159.3244				
42	*a*	897.32	0.0123	154.2677				
43	*b*	910.27		12859.6084				
44	*c*	915.03		1231.4492				
45	*c*	915.03		1257.0108				

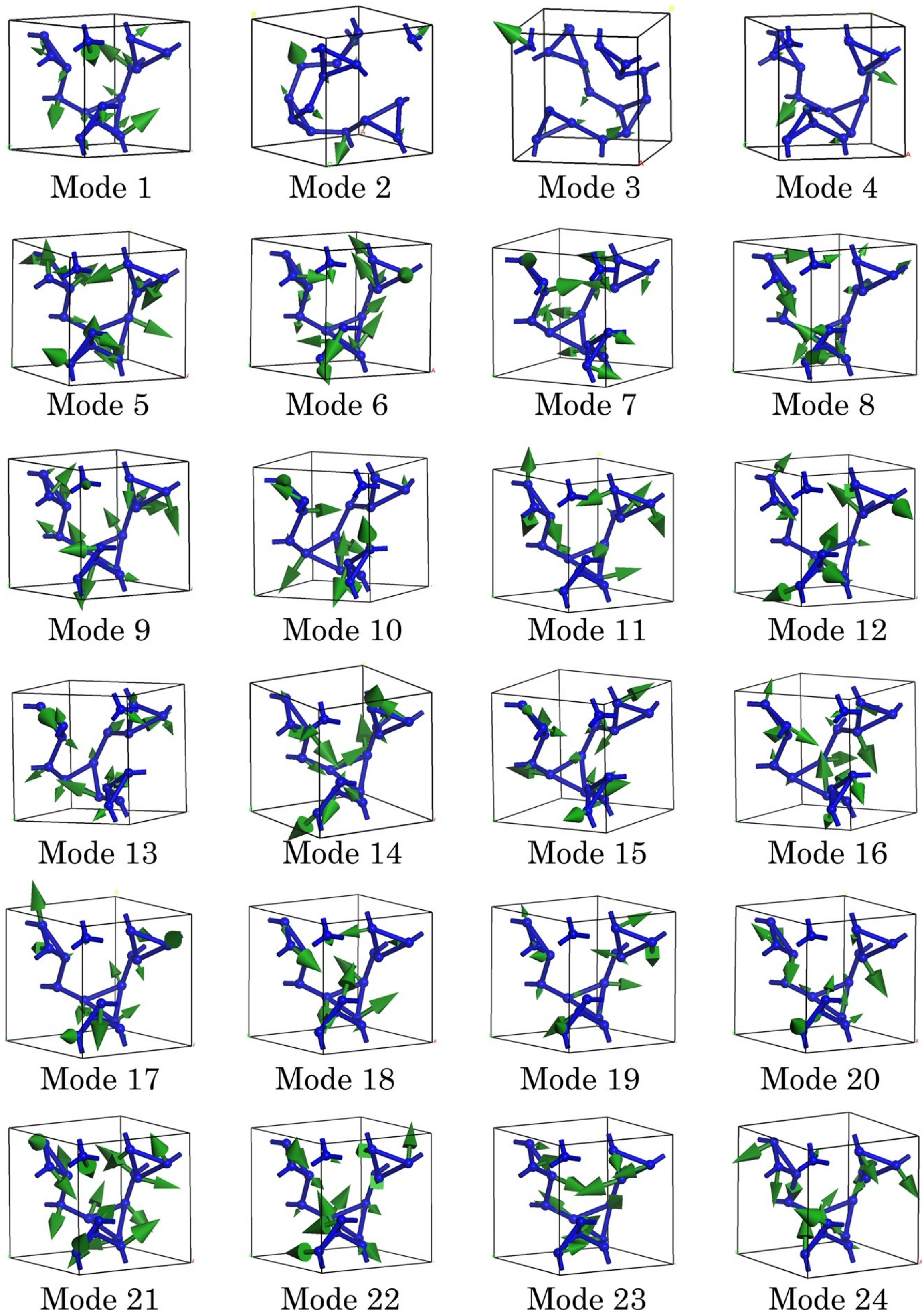


Fig. S7. Form of vibrations in the vibrational spectra of CubN and DobN.

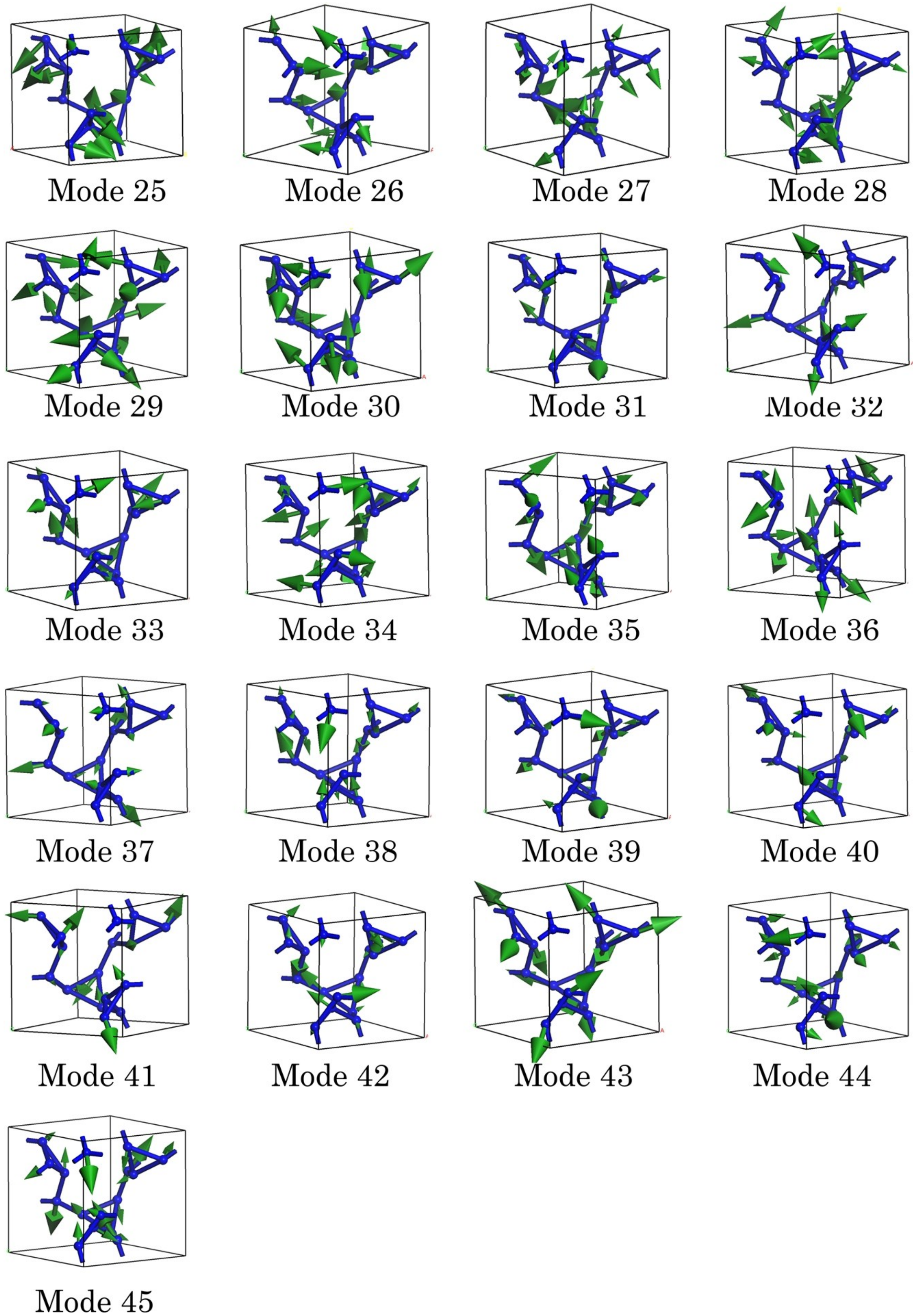


Fig. S7. (Continue).

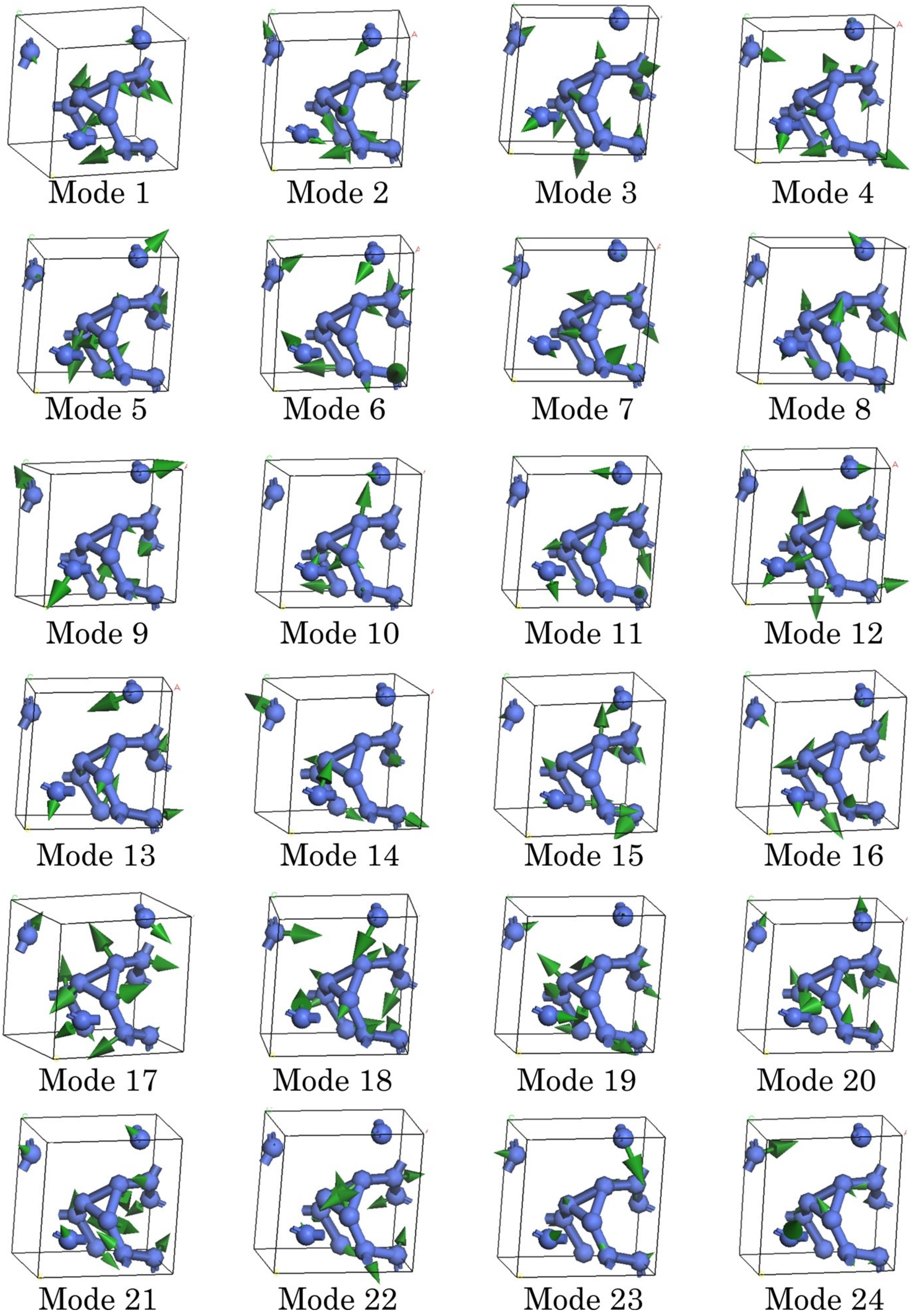


Fig. S7. (Continue).

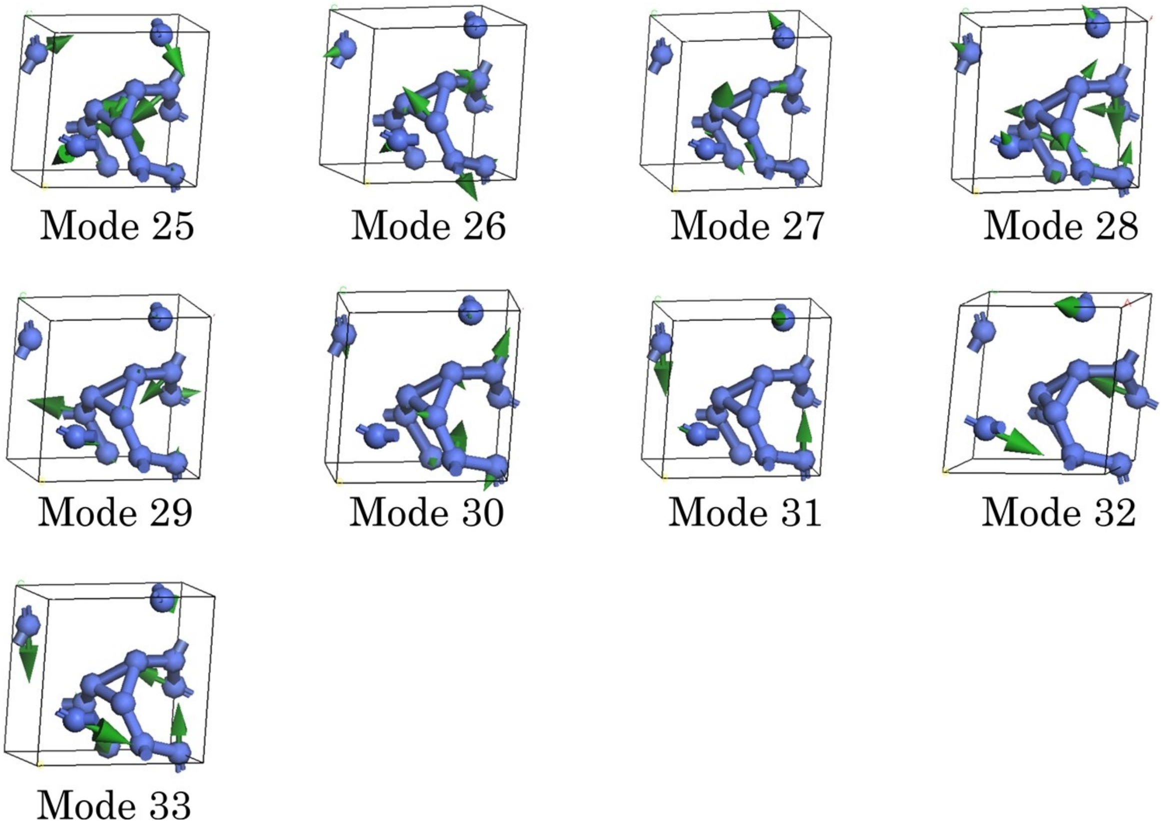


Fig. S7. (Continue).

Table S2. Chemical shielding and electric field gradient (EFG) tensors at the symmetry unique atoms in the CubN and DobN allotropes

Atom	Shielding tensor			EFG tensor	
	$\sigma_{iso}{}^{a}$ (ppm)	Δ (ppm)^{b}	η^{c}	C_Q (MHz)^{d}	$\eta_Q{}^{e}$
CubN					
N1	-21.69	-245.36	0.74	-5.077	0.74
N2	9.03	-58.87	0.00	-7.817	0.00
DobN					
N1	-138.59	-175.62	0.72	4.528	0.57
N2	-56.29	-113.81	0.37	-5.973	0.22
N3	-55.09	-303.56	0.45	-5.102	0.64
N4	-175.65	332.02	0.67	-5.216	0.28

[a] $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$.
[b] $\Delta = \sigma_{zz} - \sigma_{iso}$
[c] $\eta = (\sigma_{xx} - \sigma_{yy})/\Delta$.
[d] $C_Q = eQV_{zz}/h$, where V_{zz} is the largest component of the diagonalized EFG tensor, Q is the nuclear quadrupole moment, h is Plank's constant.
[e] $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$.

Table S3. The values of thermodynamic functions (at 298 K) for several allotropes of nitrogen

Allotrope	Z^{a}	$ZPVE^{b}$	H^{c}	G^{c}	S^{d}	$C_P{}^{e}$
cg-N	4	21.83946	1.65362	-0.60067	7.56096	17.24964
TrigN	12	22.11765	1.19821	-0.53941	5.82799	10.63478
CubN	16	18.28276	1.95812	-1.56037	11.80108	13.62955
DobN	12	19.73125	1.85304	-1.21648	10.29523	12.79239

[a]Number of atoms per asymmetric cell;
[b]Zero point vibrational energy in kJ mol^{-1} atom^{-1};
[c]The values in kJ mol^{-1} atom^{-1};
[d]The value in J mol^{-1} atom^{-1} K^{-1};
[e]The value in J mol^{-1} atom^{-1} K^{-1};

Coefficients of the NASA polynomials for the studied nitrogen allotropes in the formatted form for the CEA2 program

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cg-N                Sergey V. Bondarchuk, Jul 2019, PCCP
 2 Jul/19 N   1.00    0.00    0.00    0.00    0.00 1   14.0067000     162155.000
    200.000  1000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1653.722
 1.464961457D+05-1.722859637D+03 4.672535010D+00 8.650220080D-03-1.464428562D-05
 1.047799694D-08-2.824569895D-12 0.000000000D+00 4.764523180D+04-3.269564480D+01
   1000.000  5000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1653.722
 5.116849070D+05-2.643824933D+03 7.974976790D+00-1.440079005D-03 4.082376060D-07
-5.884210650D-11 3.379786850D-15 0.000000000D+00 5.316604330D+04-5.087714560D+01

TrigN               Sergey V. Bondarchuk, Jul 2019, PCCP
 2 Jul/19 N   1.00    0.00    0.00    0.00    0.00 1   14.0067000     172175.000
    200.000  1000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1198.335
 6.950357460D+04-8.968382530D+02 3.201964380D+00 1.888625455D-03-3.608513300D-06
 2.481505474D-09-6.098202680D-13 0.000000000D+00 4.574714400D+04-2.059626265D+01
   1000.000  5000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1198.335
 2.939526713D+05-1.368628740D+03 4.168542490D+00-7.519585170D-04 2.135749298D-07
-3.082899071D-11 1.773208535D-15 0.000000000D+00 4.881605570D+04-2.621862733D+01

CubN                Sergey V. Bondarchuk, Jul 2019, PCCP
 2 Jul/19 N   1.00    0.00    0.00    0.00    0.00 1   14.0067000     212195.000
    200.000  1000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1958.139
 8.100209800D+04-1.179547302D+03 5.859070430D+00-5.663365980D-03 7.190362790D-06
-5.195310910D-09 1.553321332D-12 0.000000000D+00 5.648520530D+04-3.406531680D+01
   1000.000  5000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1958.139
 3.683647710D+05-1.437181908D+03 4.322421640D+00-8.070353720D-04 2.303999690D-07
-3.335812020D-11 1.921484947D-15 0.000000000D+00 5.900050760D+04-2.627362644D+01

DobN                Sergey V. Bondarchuk, Jul 2019, PCCP
 2 Jul/19 N   1.00    0.00    0.00    0.00    0.00 1   14.0067000     170130.000
    200.000  1000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1853.031
 5.136501430D+04-7.659077700D+02 3.919368900D+00-2.140924671D-03 3.705942060D-06
-3.399720980D-09 1.171719169D-12 0.000000000D+00 4.435977210D+04-2.288458024D+01
   1000.000  5000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0         1853.031
 3.701397280D+05-1.515191407D+03 4.307950470D+00-8.224209220D-04 2.330125367D-07
-3.357717470D-11 1.928488807D-15 0.000000000D+00 4.935664670D+04-2.657034217D+01
```

Table S4. The coefficients *a* and *b* at various Ae/At ratios

Phase	Combustion chamber		Ae/At = 1		Ae/At = 10		Ae/At = 25		Ae/At = 50		Ae/At = 68.9	
	a	***b***	***a***	***b***	***a***	***b***	***a***	***b***	***a***	***b***	***a***	***b***
cg-N	0.5779	0.2111	0.5466	0.2267	0.3433	0.3283	0.2827	0.3587	0.2390	0.3805	0.2193	0.3903
TrigN	0.6135	0.2571	0.5826	0.2087	0.3811	0.3095	0.3206	0.3397	0.2768	0.3616	0.2571	0.3715
CubN	0.7392	0.1304	0.7100	0.1450	0.5171	0.2415	0.4582	0.2709	0.4153	0.2923	0.3959	0.3021
DobN	0.6064	0.1968	0.5754	0.2123	0.3735	0.3132	0.3130	0.3435	0.2692	0.3654	0.2495	0.3753