Supplementary Information for

**Identification of a prismatic P3N3 molecule formed from electron irradiated phosphine-nitrogen ices**

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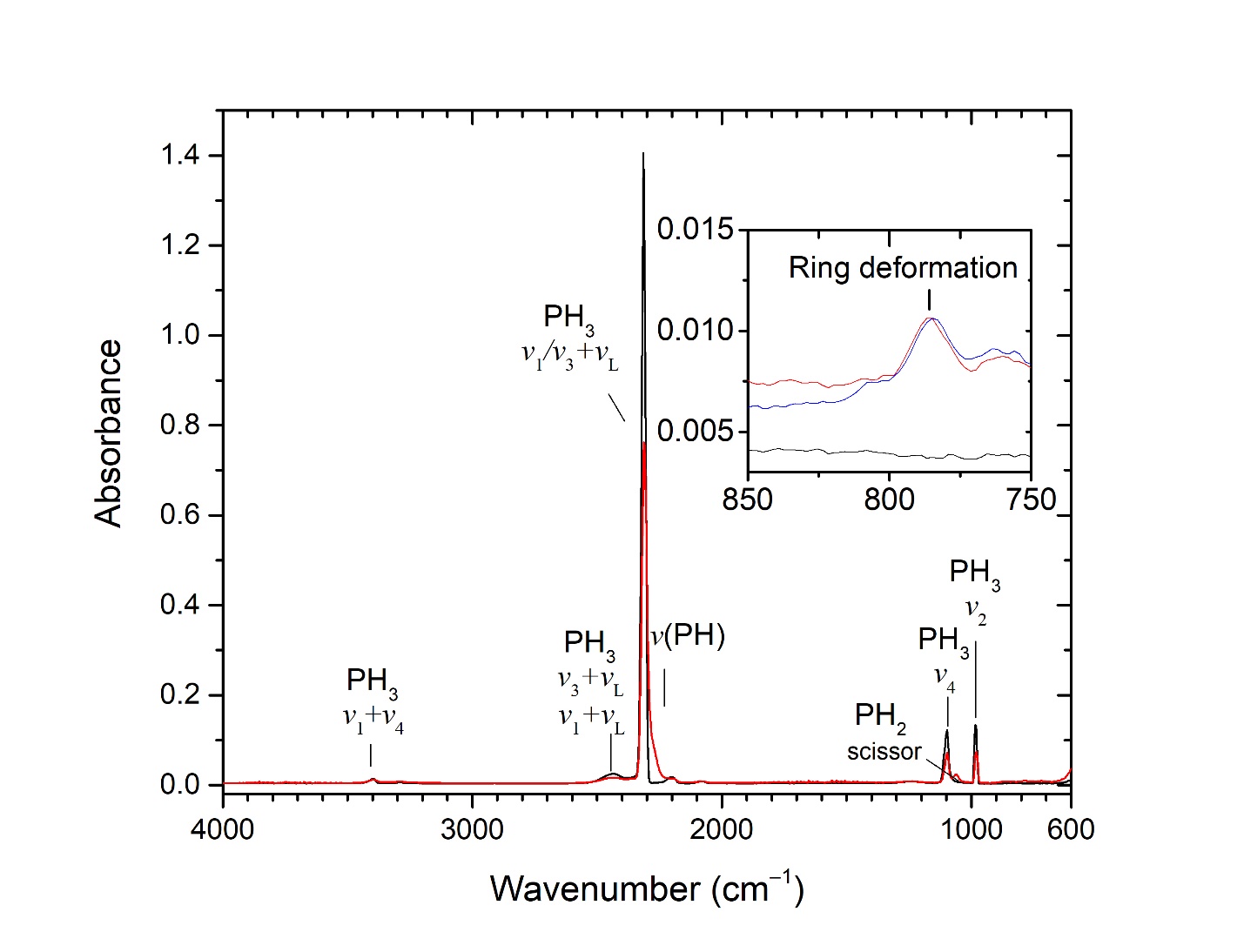
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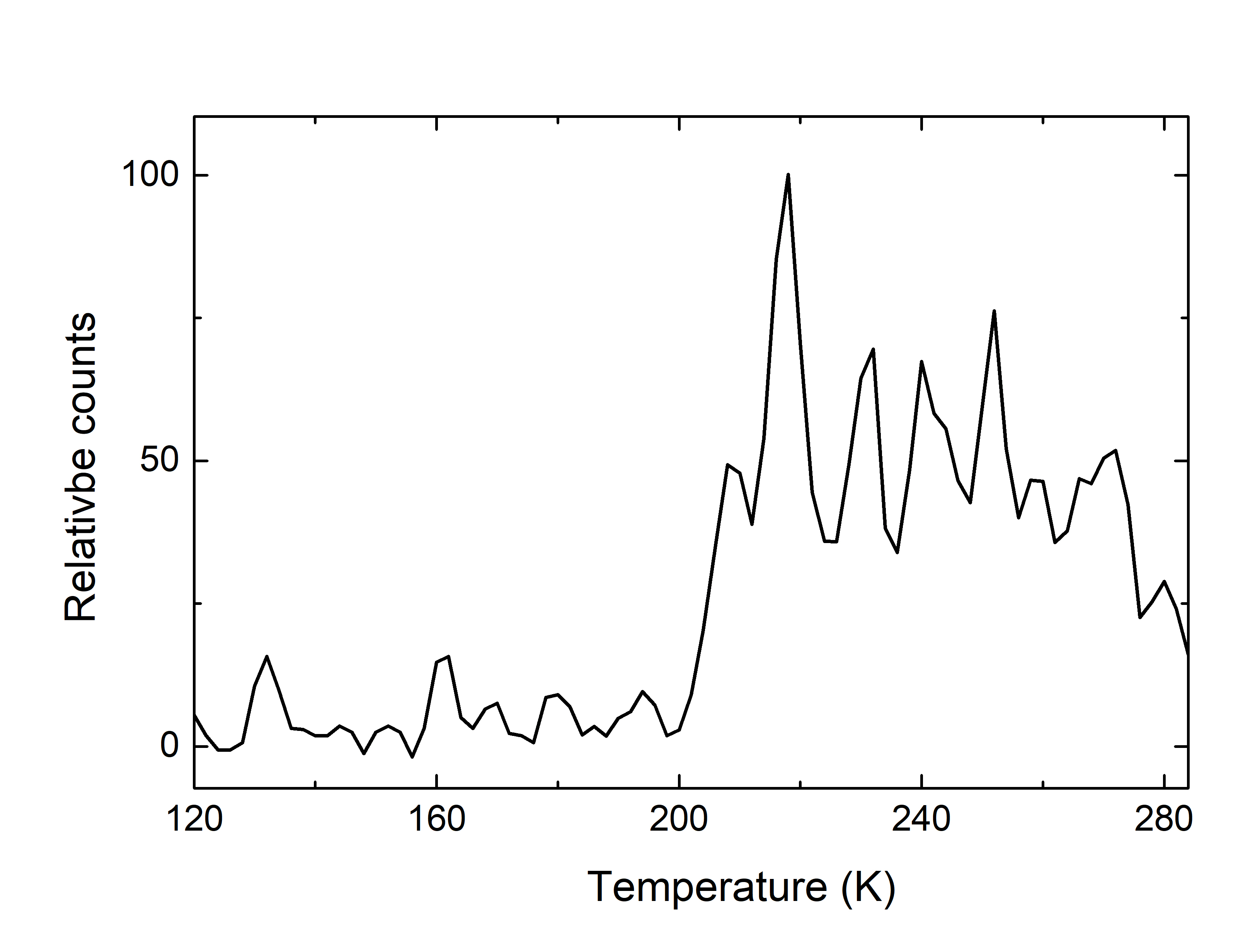
**This file includes:**

Supplementary Figures 1 and 2

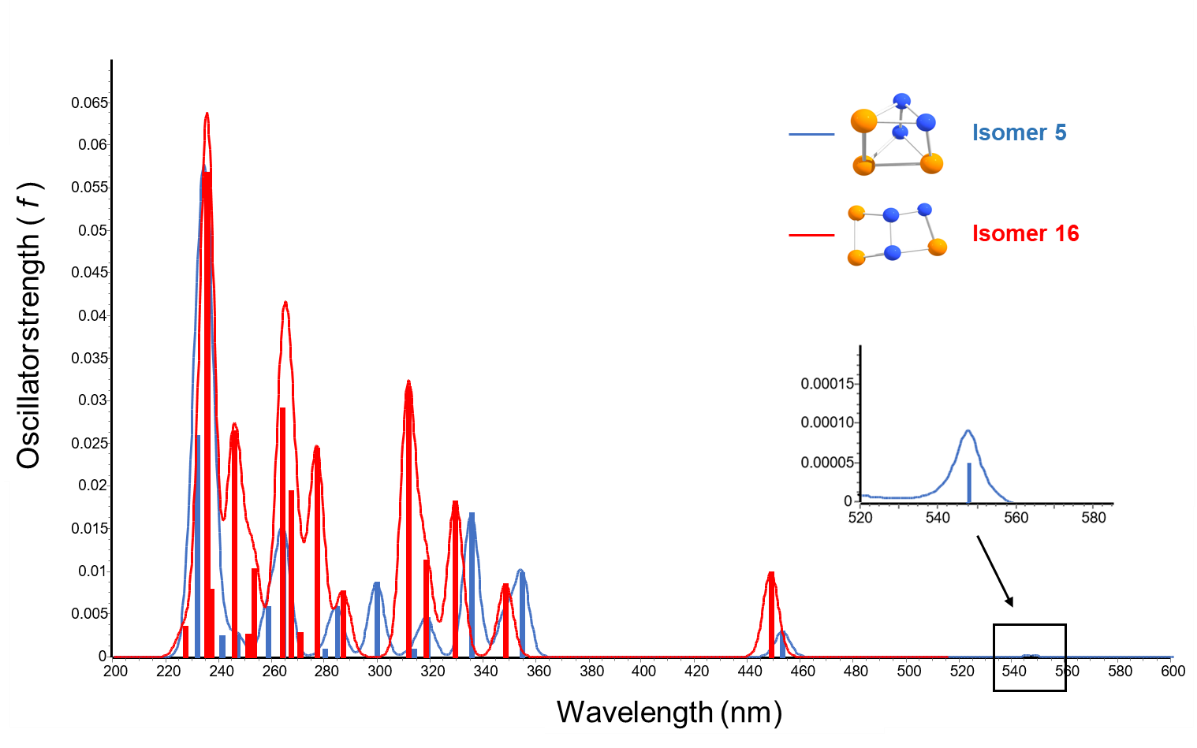
Supplementary Tables 1 to 4

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**Supplementary Figure 1.** **FTIR spectra of the phosphine (PH3) + nitrogen (N2) ice before (black) and after (red) processing with energetic electrons.** The inset expands the low-intensity region of the spectra and shows the FTIR spectrum of an electron processed phosphine (PH3) + 15N-nitrogen (15N2) ice (blue).



**Supplementary Figure 2.** **Temperature programmed desorption (TPD) profile at m/z = 138.** The data were recorded during the TPD phase of the electron processed phosphine (PH3) + 15N‑nitrogen (15N2) ice via photoionization reflectron time-of-flight mass spectrometry (PI-ReTOF-MS) at a photon energy of10.49 eV.

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**Supplementary Figure 3. Ultraviolet–visible (UV-Vis) spectra for P3N3 isomers 5 and 16.** The spectra were computed at the TD-B3LYP/cc-pVTZ level of theory.

## **Supplementary Table 1.** List of experiments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| # | Precursors | Electron current (nA) | Laser irradiation | Photoionization Energy (eV) |
| 1 | PH3 + N2 | 100 | - | 10.49 |
| 2 | PH3 + 15N2 | 100 | - | 10.49 |
| 3 | PH3 + N2 | 0 (blank) | - | 10.49 |
| 4 | PH3 + N2 | 100 | - | 8.53 |
| 5 | PH3 + N2 | 100 | - | 8.47 |
| 6 | PH3 + N2 | 100 | 547 nm | 8.47 |
| 7 | PH3 + N2 | 100 | 547 nm | 8.75 |
| 8 | PH3 + N2 | 100 | - | 8.20 |

## **Supplementary Table 2.** Data used to calculate the average irradiation dose per molecule.

|  |  |  |
| --- | --- | --- |
| Initial kinetic energy of the electrons, *Einit* (keV) | | 5 |
| Ice | | PH3 + N2 |
| Irradiation current, *I* (nA) | | 100 ± 5 |
| Total number of electrons | | (4.5 ± 0.5) × 1015 |
| Average penetration depth, *lave* (nm)a | | 490 ± 50 |
| Maximum penetration depth, *lmax* (nm)a | | 880 ± 90 |
| Average kinetic energy of backscattered electrons, *Ebs* (keV)a | | 2.96 ± 0.30 |
| Fraction of backscattered electrons, *fbs*a | | 0.12 ± 0.01 |
| Average kinetic energy of transmitted electrons, *Etrans* (keV)a | | 0 |
| Fraction of transmitted electrons, *ftrans*a | | 0 |
| Irradiated area, *A* (cm2) | | 1.0 ± 0.1 |
| Dose (eV/molecule) | PH3 | 26 ± 4 |
| N2 | 21 ± 3 |

**Note:**

a Parameters obtained using the CASINO software v2.42.

## **Supplementary Table 3.** Parameters for the vacuum ultraviolet (VUV) light generation used in the present experiments.a

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 2**1  **2 | Photoionization energy (eV) | 10.49 (3**1) | 8.75 | 8.53 | 8.47 | 8.20 |
| Flux (1011 photons s1) | 12 ± 1 | 10 ± 1 | 10 ± 1 | 10 ± 1 | 10 ± 1 |
| Wavelength (nm) | 118.222 | 141.696 | 145.351 | 146.380 | 151.200 |
| **1 | Wavelength (nm) | 355 | 202.316 | 202.316 | 202.316 | 202.316 |
| Nd:YAG (YAG A) | Wavelength (nm) | 355 | 532 | 532 | 532 | 532 |
| Dye laser (DYE A) | Wavelength (nm) | - | 606.948 | 606.948 | 606.948 | 606.948 |
| Dye |  | - | Rhodamine 610 and 640 | Rhodamine 610 and 640 | Rhodamine 610 and 640 | Rhodamine 610 and 640 |
| **2 | Wavelength (nm) | - | 353.5 | 332.5 | 327.5 | 305.5 |
| Nd:YAG (YAG B) | Wavelength (nm) | - | 532 | 532 | 532 | 532 |
| Dye laser (DYE B) | Wavelength (nm) | - | 707 | 665 | 655 | 611 |
| Dye |  | - | LDS 722 | DCM | DCM | Rhodamine 610 and 640 |
|  | Nonlinear medium | Xe | Kr | Kr | Kr | Kr |

**Note:**

a The uncertainty for VUV photon energies is 0.001 nm.

**Supplementary Table 4.** Comparison of experimental to computed ionization energies (CCSD(T)/CBS//B3LYP/cc-pVTZ + zero-point vibrational energy (ZPVE) corrections) of different nitrogen- and phosphorus- containing compounds with average deviations computed from the error limits. Combined error limits are used to obtain the corrected computed ionization energies.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compounds | Experimental IE (eV) | Experimental Error Limits (eV) | References | Computed IE (eV) | Computed IE ‒ Experimental IE (max) (eV) | Computed IE ‒ Experimental IE (min) (eV) |
| Ammonia  NH3 | 10.070 ± 0.020 | 10.050 - 10.090 | 1 | 10.15 | +0.060 | +0.100 |
| Phosphine  PH3 | 9.869 ± 0.002 | 9.867 - 9.871 | 1 | 9.82 | ‒0.051 | ‒0.047 |
| Hydrogen cyanide  HCN | 13.60 ± 0.01 | 13.59 - 13.61 | 1 | 13.57 | ‒0.04 | ‒0.02 |
| Methinophosphide  HCP | 10.79 ± 0.01 | 10.78 - 10.80 | 2 | 10.76 | ‒0.04 | ‒0.02 |
| Acetonitrile  CH3CN | 12.20 ± 0.01 | 12.19 - 12.21 | 3 | 12.20 | -0.01 | +0.01 |
| Methyl Isocyanide  CH3NC | 11.24 ± 0.01 | 11.23 - 11.25 | 3 | 11.25 | +0.00 | +0.02 |
| 2H-Azirine  c-H2CCHN | 10.05 ± 0.03 | 10.02 - 10.08 | 3 | 10.02 | 0.06 | +0.00 |
|  | | | | | Average  ‒0.04 ± 0.04 | Average  0.02 ± 0.05 |
|  | | | | | Error Limits  ‒0.08 to +0.00 | Error Limits  ‒0.03 to +0.07 |
|  | | | | | Combined Error Limits  0.08 - +0.07 | |

**Notes:**

Reference 1: Lias (2018)1.

Reference 2: Frost et al. (1973)2.

Reference 3: Turner et al. (2021)3.

**Supplementary References**

1 Sharon G. Lias, "Ionization Energy Evaluation" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <https://doi.org/10.18434/T4D303>, **2018**.

2 Frost, D., Lee, S. & McDowell, C. The photoelectron spectrum of HCP and comments on the first photoelectron band of HCN. *Chem. Phys. Lett.* **23**, 472-475 (1973).

3 Turner, A. M., Chandra, S., Fortenberry, R. C. & Kaiser, R. I. A photoionization reflectron time-of-flight mass spectrometric study on the detection of ethynamine (HCCNH2) and 2H-azirine (c-H2CCHN). *ChemPhysChem* **22**, 985-994 (2021).