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Microwave spectrum of $P^{14}N$ and $P^{15}N$: Spectroscopic constants and molecular structure

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Dedicated to Jean Demaison for his many contributions to the determination of structural and spectroscopic properties.

Abstract

In the present work the $J+1\leftarrow J$, with $J=1$–3, 6, 7, 10–16, rotational transitions of $P^{14}N$ and the $J+1\leftarrow J$, with $J=1$, 2, 7, 8, 10–14, rotational transitions of $P^{15}N$ have been observed in the millimeter- and submillimeter-wave region. These measurements allowed us to improve the ground state rotational parameters of $P^{14}N$ as well as provide those of $P^{15}N$ for the first time. The present measurements have been combined with rotational and vibrorotational transitions available in the literature to yield the Dunham coefficients. The equilibrium structure has also been determined to a high accuracy. The experimental investigation has been supported by highly accurate ab initio computations.

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1. Introduction

Only recently has the chemistry of small phosphorus-containing molecules been studied in detail, even though understanding such species is critical in a variety of areas. One of the simplest phosphorus systems is phosphorus nitride, PN, and the first spectroscopic evidence for the gaseous molecule was reported by Curry, Herzberg, and Herzberg [1]. Since its discovery, there have been a number of studies aimed at characterizing the fundamental molecular properties of this molecule (see for example Ref. [2] for a comprehensive summary).

Furthermore, the chemistry of interstellar molecules containing second-row atoms is still under investigation since only a few species of this type have actually been detected in the interstellar medium. In particular, phosphorus is of interest because little is known about its interstellar gas phase chemistry. On this subject, phosphorus nitride is the first phosphorus-bearing species observed in molecular clouds [3,4]: the detection of the $J+J\leftarrow J$, with $J=1$, 2, 3, transitions of $P^{14}N$ in different molecular clouds leaded to the identification of the first P-containing molecule [3,4]. Furthermore, in Ref. [4] it was shown that PN is likely formed by high-temperature neutral-neutral reactions and this may explain why PN was observed even if its abundance is predicted to be much lower than that of PO, which should be the most abundant phosphorus compound in cool and dense clouds.

The first observation of the rotational spectrum of $P^{14}N$ was carried out by Gordy and co-workers [5]. In Ref. [5] the measurement of several pure rotational transitions in the ground and four vibrational excited states in the millimeter- and submillimeter-wave regions by use of a high-temperature microwave spectrometer is reported. From the analysis of the data they were able to determine some Dunham coefficients, the Dunham potential constants and the equilibrium structure of PN. In the same year, Hoeft et al. investigated the $J=1\leftarrow 0$ rotational transition of the $P^{14}N$ in the ground and first vibrational excited state resolving the hyperfine structure due to the ^{14}N quadrupole coupling constant [6]. It is noteworthy that the hyperfine parameters and molecular dipole moment of $P^{14}N$ were previously accurately determined by Raymonda and Klemperer from molecular beam electric resonance

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(MBER) measurements of the $J=1$ rotational state in the $v=0$, 1, and 2 vibrational states [7]. It is interesting to notice that in all these papers PN was obtained by thermal decomposition of P_3N_5.

The first infrared study was carried out by isolating PN, again formed from P_3N_5, in a krypton matrix at 10 K [8]. The gas phase infrared spectrum was firstly observed in 1981 by Maki and Lovas at temperatures between 800 and 1050 °C using a tunable diode laser [9]. They measured vibrorotational transitions ranging from $J''=3$ to 53 and including the vibrational transitions $v' \leftarrow v''$ with $v''=0$–3; these measurements were then combined with microwave data to yield a set of ten Dunham coefficients. Subsequently, in 1995, Ahmad and Hamilton extended the $v'=1 \leftarrow 0$ measurements recording the entire band at room temperature using a Fourier transform infrared (FTIR) spectrometer [10]. They also combined their results with those previously available in order to reproduce a full set of spectroscopic parameters.

As concerns electronic transitions, it should be mentioned that in 1981 Ghosh et al. reported on the high resolution study of the $A^1\Pi$–$X^1\Sigma^+$ emission spectrum of PN in the region ranging from 2200 to 3100 Å [11].

In the present investigation the $J+1 \leftarrow J$, with $J=1$–3, 6, 7, 10–16, rotational transitions of $P^{14}N$ and the $J+1 \leftarrow J$, with $J=1$, 2, 7, 8, 10–14, rotational transitions of $P^{15}N$ have been observed in the millimeter- and submillimeter-wave region with an accuracy ranging between 5 and 80 kHz. Combining these measurements with the rotational and vibrorotational data available in the literature has made it possible to determine the Dunham constants that can be used to accurately predict the rotational transitions in excited vibrational states as well as the vibrorotational spectrum.

2. Experimental details

A frequency modulated computer-controlled spectrometer, equipped with a liquid helium-cooled InSb detector, has been used. The millimeter- and submillimeter-wave sources employed are either frequency multipliers driven by Gunn diode oscillators or Gunn diodes themselves covering the frequency range 80–800 GHz. The source is phase-locked to a Rubidium frequency standard, and the frequency modulation is obtained by sine-wave modulating the 90 MHz local oscillator of the synchronization loop. The detector output is processed by means of a lock-in amplifier tuned at twice the modulation frequency, so that the recorded profile is the second derivative of the natural line profile. A detailed description of the spectrometer is given in Ref. [12].

In regards to the experimental conditions, samples of PN have been directly prepared inside the absorption cell starting from phosphine and N_2 (approximately in the ratio 2:1) by applying a DC discharge (1500 V, 50 mA). Since PN is an unstable species, a continuous flow of gas has been ensured during the measurements by a diffusion pump in order to constantly provide fresh precursor gases and to remove final discharge products. The amount of PN prepared in such a way showed rotational spectra with a good signal to noise ratio. The rotational spectrum of $P^{15}N$ has been observed in natural abundance. Since no previous rotational constant values were available for this isotopic species, in order to confirm that $P^{15}N$ has really been detected, samples of PN have been prepared by also adding $HC^{15}N$ to the precursor gases. In this way, it was noticed that the line intensity of the rotational transitions assigned to $P^{15}N$ actually increased by one order of magnitude.

The $J+1 \leftarrow J$, with $J=1$–3, 6, 7, 10–16, rotational transitions of $P^{14}N$ and the $J+1 \leftarrow J$, with $J=1$, 2, 7, 8, 10–14, rotational transitions of $P^{15}N$ have been recorded with an accuracy ranging between 5–40 and 10–80 kHz for $P^{14}N$ and $P^{15}N$, respectively. It has to be noticed that the fine structure due to the quadrupole coupling constant of ^{14}N has been resolved for the $J+1 \leftarrow J$, with $J=1$–3, rotational transitions of $P^{14}N$.

3. Computational details

Near-equilibrium potential energy function (PEF) of PN has been calculated at different levels by accurately fitting a total of nine points to a polynomial expansion in the displacement coordinate. Spectroscopic parameters have then been determined from the fitted PEF by the usual second order perturbation theory expressions [13].

Energy evaluations have been performed with the coupled cluster singles and doubles method with a perturbative correction for connected triple excitations [CCSD(T)] [14] in conjunction with a hierarchical series of correlation consistent basis sets. More precisely, the d-augmented valence cc-pV(n+d)Z bases [15,16], with $n=Q$, 5, 6, and the weighted core-valence cc-pwCV5Z [15,17] set have been employed. In general, the frozen core approximation has been adopted in the computations, i.e. only valence electrons have been correlated. Only in the case of the core-valence basis set, calculations correlating all electrons have also been carried out. As suggested in Ref. [17], the 1s electrons of P have not been correlated in any computations.

Complete basis set limits of the total energies have been obtained by using the mixed exponential/Gaussian extrapolation formula [18,19]:

$$E(n) = E_{\mathrm{CBS}} + B\mathrm{e}^{-(n-1)} + C\mathrm{e}^{-(n-1)^2}, \qquad (1)$$

where $n=4$, 5, etc. refers to the cardinal number of the basis sets, $n=4$ for the cc-pV($Q+d$)Z basis, $n=5$ for cc-pV($5+d$)Z basis, and so on. The extrapolated total energies have then been fit as above to obtain CBS limit PEF and spectroscopic constants.

Core-valence correlation effects have been evaluated by carrying out energy computations point by point using

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