Microwave spectrum and molecular structure of PNO

Toshiaki Okabayashi, Emi Yamazaki, and Mitsutoshi Tanimoto

Department of Chemistry, Faculty of Science, Shizuoka University, 836 Oya, Shizuoka 422-8529, Japan

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The microwave spectra of $P^{14}N^{16}O$ and its isotopomers $P^{15}N^{16}O$ and $P^{14}N^{18}O$ were observed in a dc glow discharge plasma of a mixture of nitric oxide and hydrogen gases over solid red phosphorus placed on the stainless steel electrode. Rotational transitions of the parent $P^{14}N^{16}O$ species were measured in the ground state as well as in the vibrationally excited ν_1 (PN str.), ν_2 (bend), and $2\nu_2$ states. The $l=0$ substate of the $2\nu_2$ state interacts with the ν_1 state through a Fermi resonance. The rotational constants determined for the ground states of the three isotopomers yield the substitution structure, $r_s(\text{PN}) = 151.6516(87)$ pm and $r_s(\text{NO}) = 119.5025(80)$ pm. © 1999 American Institute of Physics. [S0021-9606(99)00431-6]

I. INTRODUCTION

The PNO molecule has a similar electronic configuration as the N_2O and P_2O molecules, and comparison of their molecular structures, force fields, etc. is of much interest. The N_2O molecule has been extensively studied by many high-resolution spectroscopic methods. On the other hand, knowledge of P_2O and PNO has been quite scarce because they are less stable than N_2O . Recently, however, high-resolution infrared diode laser spectroscopy^{1,2} and microwave spectroscopy³ were reported for the P_2O molecule.

The existence of the PNO molecule was confirmed by its matrix-isolated infrared spectrum,⁴ where the PNO molecule was produced by the photolysis of PN and O_3 cocondensed in an Ar matrix. The vibrational band origins were found to be $\nu_1(\text{PN str.}) = 865.2 \text{ cm}^{-1}$ and $\nu_3(\text{NO str.}) = 1754.7 \text{ cm}^{-1}$ for $PN^{16}O$, and $\nu_1 = 843.5 \text{ cm}^{-1}$ and $\nu_3 = 1727.2 \text{ cm}^{-1}$ for $PN^{18}O$. Several theoretical studies also have been carried out for the PNO molecule.⁴⁻⁹ They predicted that linear PNO is the most stable isomer among four possible structures, PNO, NPO, PON (all linear) and cyclic PNO. Quite recently, an infrared diode laser spectroscopic study was carried out by Bell *et al.*⁹ to observe the ν_3 (NO str.) fundamental and associated hot bands, in which PNO was efficiently generated by a gas-phase chemical reaction of white phosphorus vapor with O_2 and NO gases.

In the present paper, we will report the microwave spectroscopic detection of the PNO molecule in the gas phase. The rotational constants obtained for the three isotopomers ($P^{14}N^{16}O$, $P^{15}N^{16}O$, and $P^{14}N^{18}O$) were used to derive the r_0 and r_s structures. Rotational transitions were also measured in the vibrationally excited ν_1 (PN str.), ν_2 (bend), and $2\nu_2$ states for the parent $P^{14}N^{16}O$ species. The Fermi resonance between the $l=0$ substate of the $2\nu_2$ state and the ν_1 state was observed and analyzed quantitatively.

II. EXPERIMENT

The present experiment was carried out using a source modulation microwave spectrometer with a free-space discharge cell.¹⁰ Microwave radiation below 120 GHz was gen-

erated by a klystron and above 160 GHz by a multiplier following a klystron. The microwaves above 60 GHz transmitted through the 2 m long free-space cell were detected by an InSb detector cooled to 4.2 K by liquid helium. A silicon-contact crystal diode was employed to detect the microwaves below 60 GHz. The cell contained a pair of cylindrical electrodes for a dc glow discharge.

The PNO molecule was generated by a dc glow discharge in a mixture of nitric oxide (NO) and hydrogen (H_2) gases over red phosphorus powder placed on the inside of the cylindrical cathode. Although the PNO molecule contained no hydrogen atoms, the H_2 gas was indispensable for the generation of PNO. Initially, we searched for the rotational transitions of $P^{14}N^{16}O$ based on the molecular constants determined by Bell *et al.*⁹ using infrared diode laser spectroscopy. Their molecular constants were accurate enough to detect the rotational transitions easily. Subsequently, spectra of $P^{15}N^{16}O$ and $P^{14}N^{18}O$ were measured, when $^{15}N^{16}O$ and $^{14}N^{18}O$ gases, respectively, were employed instead of the normal $^{14}N^{16}O$ gas. The optimum sample pressures for PNO production were 5 mTorr of NO and 15 mTorr of H_2 . The optimum discharge current was about 20 mA. The PNO molecule was stable in the low-pressure cell made of pyrex glass, and the intensity of the PNO line did not decrease when the discharge current was dropped.

In total, we observed 160 transitions in the frequency range between 20 and 400 GHz for the three isotopomers. For the normal $P^{14}N^{16}O$ species, the spectrum was observed not only in the vibrational ground state but also in some low-lying excited states: ν_1 (PN str.), ν_2 (bend), and $2\nu_2$ states. All measurement was carried out at room temperature.

III. OBSERVED SPECTRUM AND ANALYSIS

First, the observed frequencies in each substate of a vibrational state were fitted to a standard formula for the rotational transition frequency of a linear molecule,

$$\begin{aligned} \nu_{(J+1 \leftarrow J)} = & 2B_{\text{eff}}(J+1) - 4D_{\text{eff}}(J+1)^3 \\ & + 2H_{\text{eff}}(J+1)^3(3J^2 + 6J + 4). \end{aligned} \quad (1)$$

TABLE I. Effective molecular constants of PNO.^a

Species	State	l	B_{eff} (MHz)	D_{eff} (kHz)	H_{eff} (mHz)
$\text{P}^{14}\text{N}^{16}\text{O}$	Ground ^b	0 ^c	6190.179 83(13)	1.367 891(94)	
	ν_1	0 ^c	6178.698 11(27)	1.509 25(18)	
	ν_2	1 ^e	6194.649 72(22)	1.383 93(15)	
		1 ^f	6201.957 90(16)	1.389 85(11)	
		0 ^c	6197.563 93(76)	1.165 5(12)	1.91(59)
	$2\nu_2$	2 ^e	6206.336 58(88)	1.504 5(14)	-5.22(68)
		2 ^f	6206.337 35(42)	1.405 59(28)	
$\text{P}^{15}\text{N}^{16}\text{O}$	Ground	0 ^c	6174.691 44(12)	1.363 127(86)	
$\text{P}^{14}\text{N}^{18}\text{O}$	Ground	0 ^c	5813.144 94(12)	1.198 202(79)	

^aValues in parentheses are one standard deviation.^b $B=6190.31(24)$ MHz and $D=1.39(11)$ kHz have been reported in Ref. 9.

Since perturbations by other vibrational substates are not explicitly taken into account in this treatment, the molecular constants determined here are effective constants including the perturbations. The effective constants optimized in least squares fits are listed in Table I.

In a polyatomic linear molecule, a state with an excited bending mode has several substates due to the difference in the molecular-axis component of the total vibrational angular momentum. It was necessary that l -type resonances among the l substates in the ν_2 and $2\nu_2$ state were considered in order to obtain molecular constants which were physically meaningful.

The effective rotational constants in the $2\nu_2$ state, however, exhibit anomalous behavior, which is not explained by the l -type resonances described above. The rotational constant of the $l=0$ substate, 6197 MHz, differs remarkably from that of the $l=2$ substate, 6206 MHz. In a well-behaved linear molecule, the rotational spectrum of $l=0$ and 2 substates in the $2\nu_2$ state should have similar transition frequencies. However, the transition of the $l=0$ substate of the $2\nu_2$ state is extremely shifted to lower frequency from that of the $l=2$ substate, as illustrated in Fig. 1. In other words, the effective rotational constant of the $l=0$ substate decreases 8.8 MHz from that of the $l=2$ substate. The $l=0$ substate has a Σ^+ symmetry, which is the same symmetry as the ν_1

FIG. 1. Schematic spectral pattern due to the $\text{P}^{14}\text{N}^{16}\text{O}$ molecule in the 396 GHz region. The intensity of the ground state transition is scaled down by 1/5. The anomalous shift of the $2\nu_2$ $l=0^e$ substate toward lower frequency from the $l=2$ substate is clearly illustrated.

TABLE II. Molecular constants of $\text{P}^{14}\text{N}^{16}\text{O}$ in excited vibrational states.^a

	ν_2^b	$2\nu_2$	ν_1	
B_v	6198.301 04(14)	6206.326 54(22)	6169.93795(50)	MHz
D_v	1.386 892(94)	1.405 87(16)	1.37405(38)	kHz
q_v	7.308 17(27)	7.308 17 ^c		MHz
q_{vJ}	-5.92(19)	-5.92 ^c		Hz
$d_{JL(22)}$	0.0 ^c	0.0 ^c		GHz
$x_{L(22)}$	^d	31.99(24)		GHz
ΔG_v		34.010(59)		cm^{-1}
W_F		28.051(47)		cm^{-1}

^aValues in parentheses are one standard deviation.^b $B=6198.19(35)$ MHz, $D=1.37(40)$ kHz, and $q=7.51(31)$ MHz have been reported in Ref. 9.^cFixed in the analysis.^dNot determined from rotational spectrum.

state. Since the *ab initio* calculation⁸ predicted the energy separation between the two states ($2\omega_2 - \omega_1$) as 47 cm^{-1} , it is quite probable that the ν_1 and $2\nu_2$ states are affected by each other through a Fermi resonance. Therefore, the observed transition frequencies were analyzed by a least-squares analysis using a Hamiltonian including l -type and Fermi-type resonances. The Hamiltonian employed consists of three terms,

$$H = H_{\text{vr}} + H_l + H_F, \quad (2)$$

where H_{vr} represents the vibration-rotation energy, H_l the l -type interaction energy within each vibrational state, and H_F the Fermi-type interaction energy between accidentally close states.

The matrix elements of H_{vr} and H_l are represented as follows:¹¹

$$\begin{aligned} \langle J, l | H_{\text{vr}} | J, l \rangle &= G_v + x_{L(22)} l^2 + \{B_v + d_{JL(22)} l^2\} \\ &\times [J(J+1) - l^2] - D_v [J(J+1) - l^2]^2, \end{aligned} \quad (3)$$

and

$$\begin{aligned} \langle J, l \pm 2 | H_l | J, l \rangle &= \frac{1}{4} \{q_v + q_{vJ} J(J+1)\} \sqrt{(v_2 \mp l)(v_2 \pm l + 2)} \\ &\times \sqrt{[J(J+1) - l(l \pm 1)] \{J(J+1) - (l \pm 1)(l \pm 2)\}}, \end{aligned} \quad (4)$$

where v and l are the quantum numbers of the vibration. The matrix element for the Fermi resonance is

$$\langle \nu_1 = 1, J, l | H_F | \nu_2 = 2, J, l \rangle = W_F = (1/\sqrt{2}) k_{122}, \quad (5)$$

where k_{122} is the cubic force constant. The $d_{JL(22)}$ values were fixed to 0.0 MHz in the analysis, because it was impossible to separate the contribution of the $d_{JL(22)}$ term from the Fermi resonance term. The results of the analysis are listed in Table II.

The observed transition frequencies are summarized in Tables III and IV with their final observed-minus-calculated frequencies. The standard deviation of the fit was less than

TABLE III. Observed transition frequencies in the ground vibrational state of PNO (MHz).

$J' - J''$	$P^{14}N^{16}O$		$P^{15}N^{16}O$		$P^{14}N^{18}O$	
	Obs. Freq.	O-C	Obs. Freq.	O-C	Obs. Freq.	O-C
2-1	24 760.685	0.010				
3-2	37 140.930	-0.001				
4-3	49 521.095	0.007				
5-4	61 901.116	0.002	61 746.234	0.001		
6-5	74 280.978	0.002	74 095.116	-0.004	69 756.707	0.003
7-6	86 660.636	-0.005	86 443.802	-0.008	81 382.393	0.008
8-7	99 040.082	0.006	98 792.260	-0.011	93 007.863	-0.002
9-8	111 419.253	0.005	111 140.472	0.001	104 633.120	0.005
10-9					116 258.099	-0.007
13-12	160 932.676	0.022	160 529.996	-0.002		
14-13	173 310.026	0.005	172 876.393	-0.006	162 754.901	-0.006
15-14	185 686.902	-0.026	185 222.323	-0.018	174 378.173	0.000
16-15	198 063.340	-0.003	197 567.783	-0.010	186 000.999	-0.008
17-16	210 439.221	-0.011	209 912.727	0.006	197 623.398	0.017
18-17	222 814.568	0.004	222 257.100	0.007	209 245.279	0.013
19-18	235 189.310	0.006	234 600.881	0.005	220 866.646	0.012
20-19	247 563.433	0.013	246 944.045	0.007	232 487.433	-0.022
21-20	259 936.878	-0.003	259 286.553	0.008	244 107.712	0.011
22-21	272 309.656	0.005	271 628.359	-0.006	255 727.326	-0.018
23-22	284 681.697	-0.003	283 969.464	-0.002	267 346.364	0.011
24-23	297 052.979	-0.014	296 309.818	0.004	278 964.685	-0.017
25-24	309 423.503	0.005	308 649.387	0.010	290 582.359	-0.001
26-25	321 793.167	-0.016	320 988.128	0.006	302 199.289	-0.010
27-26			333 326.036	0.020	313 815.498	0.008
28-27					325 430.915	0.010
29-28	358 896.983	-0.001	357 999.104	-0.019		
30-29	371 263.059	0.002	370 334.268	-0.001		
31-30	383 628.162	0.016	382 668.436	0.002	360 272.206	0.002
32-31	395 992.211	-0.006	395 001.575	-0.010	371 884.223	-0.003
33-32					383 495.322	-0.005
34-33					395 105.485	0.005

30 kHz for the ground and vibrationally excited states of each isotopomer, which roughly corresponds to the accuracy of measurement.

IV. RESULTS AND DISCUSSION

The vibrational dependence of the rotational constants B_v is expressed by

$$B_v = B_e - \sum_i \alpha_i \left(v_i + \frac{d_i}{2} \right) + \sum_i \sum_j \gamma_{ij} \left(v_i + \frac{d_i}{2} \right) \left(v_j + \frac{d_j}{2} \right). \quad (6)$$

The deperturbed vibration-rotation constants are derived from the rotational constants of the ground, v_1 and v_2 states as $\alpha_1 = 20.24188(52)$ MHz and $\alpha_2 = -8.121\,21(19)$ MHz, when the higher-order terms γ_{ij} are omitted. These α values are in good agreement with those predicted by the *ab initio* calculation,⁸ $\alpha_1 = 19.53$ MHz and $\alpha_2 = -8.05$ MHz, as listed in Table V. The α_3 value has been already determined to be 27.521(90) MHz by the infrared diode laser spectroscopy,⁹ but it is quite different from the *ab initio* value of 43.16 MHz.⁸ This discrepancy is probably caused by the complicated Fermi resonance system $[(2v_1) \sim (v_1 + 2v_2) \sim (4v_2) \sim (v_3)]$ as suggested in Refs. 8 and 9.

The l -type doubling constant q_2 is obtained to be 7.30817(27) MHz in the present analysis. Pak and Woods⁸

predicted the equilibrium l -type doubling constant $q_e = 7.11$ MHz, which is consistent with our experimental value. They also predicted the equilibrium centrifugal distortion constants $D_e = 1.32$ kHz, which agrees well with our D_0 value of 1.36891(94) kHz.

In the $2v_2$ state, the energy separation between the $l = 0$ and $l = 2$ substates is represented by $4x_{L(22)}$. A positive $x_{L(22)}$ value indicates that the $l = 0$ substate is located below the $l = 2$ substate. Under the deperturbed condition, $x_{L(22)}$ is obtained to be 1.0670(79) cm^{-1} from a least-squares fit. This value is different from the *ab initio* prediction of -0.20 cm^{-1} (Ref. 8) in their signs, but these two values are consistent in their small absolute magnitude. If the perturbation by the Fermi resonance is not considered, the value of $x_{L(22)}$ is calculated to be about -4 cm^{-1} , which is in good agreement with the *ab initio* value of -3.63 cm^{-1} .⁸ The perturbed $x_{L(22)}$ value decreases by about 5 cm^{-1} from the unperturbed one through the Fermi resonance. In other words, the $l = 0$ substate is pushed up about 20 cm^{-1} by the Fermi interaction. The cubic force constant k_{122} is obtained to be 39.670(67) cm^{-1} from the W_F value using Eq. (5), which is consistent with the value of the *ab initio* calculation of 35.944 cm^{-1} .⁸

The r_0 structure is determined from the rotational con-

TABLE IV. Observed transition frequencies in excited vibrational states of $P^{14}N^{16}O$ (MHz).

$J' - J''$	ν_1		ν_2 ($l=1^e$)		ν_2 ($l=1^f$)	
	Obs. Freq.	O-C	Obs. Freq.	O-C	Obs. Freq.	O-C
16-15			198 206.116	-0.001	198 439.884	0.003
17-16	210 046.093	-0.001	210 590.894	0.000	210 839.252	-0.003
18-17	222 397.930	-0.008	222 975.115	0.009	223 238.049	-0.013
19-18	234 749.125	-0.005	235 358.722	0.002	235 636.281	0.013
20-19	247 099.608	-0.025	247 741.691	-0.012	248 033.859	0.018
21-20	259 449.433	0.021	260 124.013	-0.009	260 430.753	0.007
22-21	271 798.444	0.013	272 505.626	-0.017	272 826.941	-0.010
23-22	284 146.636	-0.017	284 886.544	0.010	285 222.416	-0.006
24-23	296 494.041	-0.001	297 266.656	-0.005	297 617.117	-0.009
25-24	308 840.587	0.024	309 646.013	0.023	310 010.909	-0.120 ^a
26-25	321 186.189	0.009	322 024.490	0.000	322 404.101	0.002
29-28	358 217.249	0.005	359 154.683	0.010	359 577.968	-0.002
30-29	370 558.869	-0.015	371 529.530	0.011	371 967.363	-0.007
31-30	382 899.433	-0.007	383 903.337	-0.031	384 355.763	-0.007
32-31	395 238.882	0.005	396 276.195	0.008	396 743.149	0.014
	$2\nu_2$ ($l=0^e$)		$2\nu_2$ ($l=2^e$)		$2\nu_2$ ($l=2^f$)	
17-16	210 694.281	-0.005	210 985.846	0.007	210 987.856	-0.001
18-17	223 085.132	-0.002	223 392.950	-0.014	223 395.348	-0.016
19-18	235 475.478	-0.003	235 799.426	-0.009	235 802.280	0.016
20-19	247 865.285	-0.012	248 205.202	-0.013	248 208.481	-0.043
21-20	260 254.564	0.008	260 610.292	0.024	260 614.127	0.019
22-21	272 643.249	0.019	273 014.570	0.012	273 018.980	-0.004
23-22	285 031.279	-0.012	285 418.053	0.006	285 423.118	0.001
24-23	297 418.714	0.003	297 820.745	0.046	297 826.432	-0.043
25-24	309 805.479	0.016	310 222.496	0.020	310 229.055	0.033
26-25	322 191.519	0.000	322 623.342	0.001	322 630.683	-0.044
29-28	359 345.239	0.000	359 820.091	-0.009	359 830.437	-0.003
30-29	371 728.223	-0.015	372 216.942	-0.007	372 228.453	0.020
31-30	384 110.383	-0.021	384 612.710	0.009	384 625.421	0.008
32-31	396 491.733	0.023	397 007.287	-0.031	397 021.358	0.010

^aNot weighted.

stants of $P^{14}N^{16}O$, $P^{15}N^{16}O$, and $P^{14}N^{18}O$ in the ground state using a least-squares method. The obtained bond lengths are $r_0(PN) = 152.50(16)$ and $r_0(NO) = 118.99(20)$ pm. The r_s structure is also determined from the rotational constants in the ground state of the three isotopomers using Kraitchman's equation.¹² The derived bond lengths are $r_s(PN)$

$= 151.6516(87)$ and $r_s(NO) = 119.5025(80)$ pm, where the uncertainties are primarily derived from errors of Planck and Avogadro constants.

Table VI compares the experimental and theoretical molecular structure of PNO. The SCF results with any basis functions are somewhat shorter than the experimental values. On the contrary, the CAS-SCF, MP2, and MP4SDTQ methods result in apparently longer PN length. Other high level calculations (CISD, CCSD, and B3LYP) give better internuclear distances. Although PNO is a simple linear molecule, the high level calculation is needed to reproduce the experimental values.

The PNO and N_2O molecules have conjugated structure including "acetylene-like" and "allene-like" structures as follows:

Since oxygen possesses much larger electronegativity than phosphorus, the acetylene-like structure is probably dominant in the PNO molecule. On the other hand, the acetylene-like and allene-like structures seem to be competitive in the N_2O molecule, as is inferred from the small dipole moment of N_2O , 0.16 D.¹⁶ Therefore, it is reasonable that the NO

TABLE V. Comparison between experimental and theoretical parameters of PNO.

	Experimental ^a	Theoretical ^b	
B_0	6190.179 83(13)	6148.8, 6195.1 ^c	MHz
α_1	20.241 88(52)	19.53	MHz
α_2	-8.121 21(19)	-8.05	MHz
α_3	27.521(90) ^{d,e}	43.16	MHz
D_0	1.36 789 1(94)	1.32 (D_e)	kHz
q_2	7.308 17(27)	7.11 (q_e)	cm ⁻¹
ΔG_v	34.010(59)	47 ($2\omega_2 - \omega_1$)	cm ⁻¹
$x_{L(22)}$	1.067 0(79)	-0.20	cm ⁻¹
$x_{L(22)}^d$	-4.070 6(70)	-3.63	cm ⁻¹
k_{122}	39.670(67)	35.944	cm ⁻¹

^aThis work.^bReference 8.^c $B_0 = B_e - \sum_i \alpha_i (v_i + d_i/2)$.^dPerturbed value.^eReference 9.

TABLE VI. Molecular structures of PNO and related molecules (pm).

Molecule		$r(\text{PN})$	$r(\text{NO})$	Methods	Ref.
PNO	r_0	152.50(16)	118.99(20)	MW	This work.
	r_s	151.651 6(87)	119.502 5(80)	MW	This work.
	r_e	149.16	116.71	SCF/DZP	4
	r_e	152.3	119.4	CISD/TZ2P+ f	4
	r_e	148.6	116.3	SCF/DZP	5
	r_e	148.5	117.6	SCF/DZP	6
	r_e	148.0	116.2	SCF/TZ2P	6
	r_e	151.2	119.5	CISD/DZP	6
	r_e	150.4	117.5	CISD/TZ2P	6
	r_e	152.9	120.7	CCSD/DZP	6
	r_e	155.1	120.4	CAS-SCF/DZP	6
	r_e	148.17	116.94	SCF/6-31G**	7
	r_e	157.47	120.44	MP2/6-31G**	7
	r_e	157.27	122.82	MP4SDTQ/6-31G**	7
	r_e	152.88	118.98	CCSD(T)/cc-pVQZ	8
	r_e	152.1	118.8	CCSD(T)/cc-pVQZ[Corrected]	8
	r_e	152.51	119.72	B3LYP/6-31+G(d)	9
	r_e	151.78	118.88	B3LYP/6-311+G(2 d , p)	9
	r_e	151.62	118.65	B3LYP/6-311+G(2 df ,2 p)	9
N ₂ O	r_s		118.46	MW	13
	r_e		118.41(3)	IR	14
PN	r_s	149.086(2)		MW	15
	r_e				

bond length in PNO is somewhat greater than in N₂O. However, since the contribution of the allene-like structure is not negligible for PNO as well, the PN bond length of PNO is longer than that of the diatomic P≡N molecule.

Since nitrogen nucleus possesses a nuclear quadrupole moment, we tried to observe the hyperfine splitting in the $J=2-1$ transition at the 25 GHz region, which was close to the lowest frequency available for our spectrometer. However, no splitting was seen in the observed spectrum as illustrated in Fig. 2. The full width at half maximum (FWHM) of the observed line was about 0.2 MHz. If the hyperfine splitting is smaller than 0.2 MHz, the nuclear quadrupole coupling constant $|eQq|$ of nitrogen should be less than about 0.5 MHz. This value is roughly consistent with the eQq value due to the central nitrogen of N₂O, -0.2694 MHz,¹⁷ and somewhat smaller than that of terminal nitrogen of N₂O, -0.7767 MHz (Ref. 17) in their absolute values.

FIG. 2. $J=2-1$ rotational transition of P¹⁴N¹⁶O in the vibrational ground state observed near 25 GHz. The splitting due to the nitrogen nuclear quadrupole coupling effect is not resolved. The accumulation time is about 33 min.

In the present experiment, H₂ was indispensable for the generation of PNO from red phosphorus and NO gas. Since the PNO molecule contains no hydrogen atom, the H₂ gas probably behaves as a catalyst. A similar phenomenon was reported in the case of the generation of the PO radical from red phosphorus and O₂.¹⁸ It is implied that red phosphorus initially reacts with hydrogen atoms and that phosphorus hydrides PH_{*n*} ($n=1-3$) produced in the initial step are probably oxidized in the subsequent steps. Similar reactions seem to occur in the case of PNO generation from activated solid red phosphorus.

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