Ab initio study and millimeter-wave spectroscopy of P_2O

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The millimeter-wave spectrum of P_2O produced by reacting P_4 vapor with atomic or molecular oxygen directly inside the absorption cell has been observed in 13 vibrational states. Reliable identification of the various vibrationally excited states has been achieved with the help of high-level *ab initio* calculations resulting in accurate geometric data and an anharmonic force field. Careful analysis of the vibrational levels observed resulted in 13 sets of rotational and centrifugal distortion parameters, which have been used, in turn, to determine the equilibrium rotational, quartic centrifugal distortion, and rovibrational interaction constants of P_2O. The $2\nu_1-\nu_3$ Fermi resonance has been analyzed. © *1997 American Institute of Physics.* [S0021-9606(97)01137-9]

I. INTRODUCTION

Interest in the gas-phase chemistry of phosphorus is related to environmental preoccupations,[1] its role in interstellar and circumstellar chemistry,[2–4] and problems concerning the mechanism of its chemical oxidation.[5,6] Accordingly, a number of experimental[7–15] and theoretical[16–27] studies have been devoted to the characterization of small phosphorus-containing molecules.

Until quite recently, it was customary to regard the bonding properties of first row elements as normal and to consider the structural behavior of their heavier analogs as "abnormal." It is now well established that perhaps the higher row elements behave normally and those from the first row are anomalous.[28] To aid structural comparison of first- and related second-row compounds, several high resolution spectroscopic studies have been performed in Lille on small molecules (HNSi,[29] Si_2H_2,[30,31] H_2SiO,[32] and H_2CSiH_2).[33]

Diphosphorus oxide, P_2O, is related to the well characterized molecule N_2O.[34] In the 1990's, several studies using various techniques of molecular electronic structure theory have been published on P_2O.[22–27] Lohr[22] investigated the structural isomers of several gaseous diphosphorus oxides (P_2O_x, $x=1-5$) at introductory self-consistent-field (SCF) levels. Energy calculations performed at the SCF and fourth-order Møller–Plesset [(MP4)(SDTQ)] levels established the linear form of P_2O ($\widetilde{X}\ {}^1\Sigma^+$) to be considerably more stable than the triangular form (${}^1A_1$) with electron correlation stabilizing the linear form. Both the linear and the triangular isomers appeared to be minima on the potential energy surface (PES) of P_2O. Jarrett–Sprague and co-workers[23] determined optimized geometries and harmonic vibrational frequencies of several P_xO_y compounds at the SCF and MP2 levels. Scaling of the quadratic force fields within the scaled quantum mechanical (SQM) force field scheme[35,36] has also been attempted resulting in rather accurate frequency predictions. Davy *et al.*,[24] within the framework of a high-level theoretical study of HP_2O^+, reported detailed structural and energetic results on the $\widetilde{X}\ {}^1\Sigma^+$, ${}^1A_1$, and ${}^3B_2$ electronic states of P_2O. Ornellas and Aquino[25] employed multireference configuration interaction (MR-CI) calculations for the study of the singlet state of P_2O and examined several dissociation channels, as well. Blaszkowski and Nascimento[26] used the generalized valence bond (GVB) and GVB-CI techniques in a detailed investigation of the nature of the chemical bonds in P_2O. Both studies concluded that the existence of a fully repulsive ${}^3\Pi$ excited electronic state which crosses the ground state PES at relatively low energy would provide a dissociation channel for the molecule at higher temperatures and thus explains the failure to detect P_2O under normal circumstances. Aquino and Taylor[27] characterized P_2O^+ by means of *ab initio* calculations and reported bond lengths, harmonic frequencies, and dissociation energies for the linear form of P_2O. In this latter work, some calculations have been performed at the cc-pVTZ CCSD(T) level employed extensively in this study.

P_2O was first detected in a matrix,[10,11] where it was formed through a reaction between oxygen atoms and white phosphorus P_4. Using a similar technique of production, Qian *et al.*[15] observed some *P* and *R* infrared lines of this molecule in the gas phase. Recently, more extensive measurements of the ν_3 and $\nu_3+\nu_2\leftarrow\nu_2$ band were performed as described in the accompanying article.[37]

In this article, we present accurate measurements of the rotational spectra of P_2O, produced by a chemiluminescent reaction between the vapor of white phosphorus P_4 and atomic or molecular oxygen, in various vibrational states. Identification of the spectral lines observed proved to be impossible without the help provided by *ab initio* calculations resulting on equilibrium geometry and the anharmonic force field of the molecule.

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II. EXPERIMENTAL AND THEORETICAL DETAILS

Since the millimeter-wave spectrometer used in this study and its improvements have been described in detail previously,[30,38] only the most relevant aspects of these experiments will be discussed here.

Up to 340 GHz, the millimeter-wave power was obtained by harmonic generation from phase-locked Varian klystrons using Schottky barrier diodes mounted in a commercial Custom Microwave multiplier. Above 340 GHz, two Thomson CSF backward-wave oscillators (BWO) emitting in the 340–475 GHz frequency range have been employed. They were phase locked on the emission of a 12–18 GHz Giga Instrument synthesizer. The high output level of these BWO allowed an improved sensitivity in this frequency range, typically 10^{-8} cm^{-1} for a 10 Hz bandwidth. Detection of the spectral lines has been achieved with a helium cooled InSb detector from QMC Instrument. Source modulation at 40 kHz and lock-in detection at 80 kHz provided a second derivative line shape. A Hewlett–Packard microcomputer ensured frequency scanning, data acquisition, signal processing, and frequency measurement. Under these conditions, the estimated experimental error on the frequency measurement appears to be less than 50 kHz, except for lines with a very poor signal-to-noise ratio.

The absorption cell consisted of a 2 m long, 5 cm i.d. pyrex tube connected on one side to the vacuum pumping system, and on the other side to a cross-shaped glass part. Both ends of the cell were closed by two Teflon windows at Brewster incidence to reduce standing waves. Oxygen was introduced through one side arm of the cross-shaped part, equipped with a 2450 MHz cavity. P_4 vapor seeded in an argon flow was injected through the opposite side arm. Solid white phosphorus cut into small pellets, typical size $3\times3\times3$ mm^3, was stored in a glass container and used without heating, the P_4 vapor pressure being of the order of $3-4\times10^{-2}$ mbar at room temperature. The white phosphorus had to be changed regularly, due to contamination and surface oxidation. The mixing region of the cell could be cooled by flowing liquid nitrogen through a rubber tube wound around it.

In our first experimental setup, atomic oxygen was produced by a 2450 MHz discharge in O_2. It was mixed with P_4 and Ar, the cell being cooled by liquid nitrogen. This cooling was not essential but led to a better signal-to-noise ratio. A moderate microwave power of the order of 30–40 W was coupled to the oxygen plasma. Under these conditions, the optimum partial pressures were 7×10^{-3} mbar O_2 and 8×10^{-2} mbar P_4+Ar. During the second set of experiments, the strongest absorption signals of P_2O have been observed without microwave discharge and without cooling: molecular oxygen with slightly increased partial pressure up to 10^{-2} mbar was simply mixed in the cell with white phosphorus vapor and argon. In the mixing region, a chemiluminescence was observed. During these experiments, a orange-red deposit has been observed on the inner surface of the cell. The absorption signals of P_2O critically depended on the experimental conditions: flow speed, partial pressures, and deposits inside the cell. In all cases, P_2O was produced in low concentration and the experimental conditions had to be adjusted very carefully in order to make the detection of the spectral lines belonging to P_2O possible, even if, with a calculated dipole moment of nearly 1.7 D, the line intensities should be rather large.

The basis sets selected for this study include the TZ2P and QZ2P basis sets of Ahlrichs,[39] and the cc-pVTZ basis set of Dunning and co-workers.[40] Only the pure spherical components of the basis functions have been employed. Electronic wave functions have been determined at several different levels: self-consistent-field restricted Hartree–Fock (SCF),[41,42] second-order Møller–Plesset (MP2),[43] coupled-cluster singles and doubles (CCSD),[44] the CCSD level including a perturbative estimation of connected triples,[45] abbreviated as CCSD(T), and a density functional theory (DFT) approximation usually abbreviated as B3LYP.[46,47] Geometry optimizations have been performed employing analytic geometric first derivatives at all levels. No orbitals have been kept frozen during the calculations. All *ab initio* computations have been performed with the program systems ACESII[48] and GAUSSIAN94.[47]

III. THEORETICAL STRUCTURAL RESULTS

Calculated geometries of the two different stable forms of P_2O, linear and triangular, are presented in Table I, together with relative energy estimates of the two forms. The anharmonic (quartic) force field of P_2O, determined at the cc-pVTZ CCSD(T) level of *ab initio* theory, is presented in Table II both in an internal coordinate and in a normal coordinate representation (the latter for $^{31}P_2{}^{16}O$). It has been obtained from altogether 19 analytic force calculations at distorted geometries employing the {stre, stre, bend} set of internal coordinates and displacement sizes of ±0.02 Å and 0.02 rad. The reference geometry chosen for the force field calculation corresponds to the optimized equilibrium geometry obtained at the same level [cc-pVTZ CCSD(T)] for two reasons: (a) to avoid the difficulties[49] arising from the choice of a nonstationary reference geometry; and (b) it has been demonstrated several times[50,51] that at this level of theory there is a particularly advantageous error cancellation resulting in apparently highly accurate (anharmonic) force fields and subsequent vibrational frequency predictions. The cc-pVTZ CCSD(T) quartic force field determined should give[50–53] a very good representation of the electronic ground state potential energy surface (PES) of P_2O around the true equilibrium structure. Breakdown of the Born–Oppenheimer approximation, on which the concepts of geometry and PES are based, as well as neglect of relativistic effects during the calculations, are expected to produce only marginal changes in the force constants. Therefore, almost all remaining errors in the force field should be assigned to core-core and core-valence correlation effects, not considered explicitly in this study. These have repeatedly been shown[51,52] to be very important when the calculated anharmonic force field was to approach the ultimate computational result. *Ab initio* values for the equilibrium and ground state rotational constant, the

TABLE I. Theoretical structural results (r/Å) and relative energies (ΔE/cm^{-1}) of the linear ($\widetilde{X}^1\Sigma^+$) and triangular ($^1A_1$) forms of P_2O.[a]

Method	Linear r(PP)	Linear r(PO)	Triangular r(PP)	Triangular r(PO)	ΔE	Reference
3-21G* SCF	1.841	1.452	1.934	1.736	1699	22
6-31G* SCF	1.852	1.446	1.939	1.726	1876	22
TZ2P/DZP SCF	1.854/1.851	1.438/1.446	1.933/1.937	1.717/1.721	4370/2921	24
cc-pVTZ B3LYP	1.896	1.480	1.977	1.755	3746	this work
6-31G* MP2	1.922	1.503	2.012	1.776	3643	23
cc-pVTZ MP2	1.920	1.490	2.001	1.762	5120	this work
DZP CASSCF	1.904	1.497	2.035	1.784	4633	24
TZP CASSCF	1.915	1.510	⋯	⋯	⋯	27
TZ2P/DZP CISD	1.878/1.874	1.459/1.477	1.960/1.963	1.741/1.747	3768/2515	24
DZP CCSD	1.894	1.485	1.995	1.764	1870	24
TZ2P CCSD(T)	1.918	1.483	2.017	1.760	3852	this work
QZ2P CCSD(T)	1.916	1.485	2.012	1.754	3149	this work
cc-pVTZ CCSD(T)	1.904	1.481	1.998	1.751	3638	this work

[a] The relative energies are given as E(triangular)-E(linear).

centrifugal distortion constant, the rotation-vibration parameters, and the l-type doubling constant are given in Table III. Harmonic vibrational frequencies and vibrational anharmonicity constants are presented in Table IV. Precision of the quartic force field of P_2O determined can be appreciated from the following: (a) the two measured[37] vibrational levels of P_2O (see Table IV) are reproduced with an average error of only 1.1 cm^{-1}; and (b) the accuracy is comparable for the prediction of the only two spectroscopic constants available experimentally, the quartic centrifugal distortion constant D_J (Table III), and the vibrational anharmonicity constant x_{23} (Table IV).

TABLE II. Complete quartic force field of P_2O.[a]

Constant	In internal coordinates	Constant	In normal coordinates
f_{RR} (PP)	5.210	ω_1	658.3
f_{Rr}	-0.050	ω_2	211.5
f_{rr} (PO)	9.544	ω_3	1295.7
$f_{\alpha\alpha}$	0.314	ϕ_{111}	-145.2
f_{RRR}	-26.301	ϕ_{113}	45.7
f_{RRr}	0.160	ϕ_{122}	50.0
f_{Rrr}	-0.135	ϕ_{133}	-127.7
f_{rrr}	-61.084	ϕ_{223}	173.7
$f_{\alpha\alpha\mathrm{R}}$	-0.910	ϕ_{333}	-339.9
$f_{\alpha\alpha\mathrm{r}}$	-0.364	ϕ_{1111}	26.1
f_{RRRR}	101.297	ϕ_{1113}	-10.8
f_{RRRr}	0.672	ϕ_{1122}	-12.1
f_{RRrr}	0.359	ϕ_{1133}	12.4
f_{Rrrr}	0.960	ϕ_{1223}	-11.7
f_{rrrr}	327.171	ϕ_{1333}	21.2
$f_{\alpha\alpha\mathrm{RR}}$	0.527	ϕ_{2222}	81.7
$f_{\alpha\alpha\mathrm{Rr}}$	0.990	ϕ_{2233}	-78.2
$f_{\alpha\alpha\mathrm{rr}}$	0.022	ϕ_{3333}	94.9
$f_{\alpha\alpha\alpha\alpha}$	0.389		

[a] Units of the internal coordinate force constants are consistent with the energy measured in aJ, the stretching motions (**r** and **R**) in Å, and the bending motions (α) in rad. The normal coordinate force constants in cm^{-1} refer to $^{31}P_2{}^{16}O$. The force field has been determined at the cc-pVTZ CCSD(T) level.

IV. EXPERIMENTAL OBSERVATIONS

During the first searches for the rotational spectrum of P_2O, using the reaction between P_4 and atomic oxygen to produce the molecule, we scanned a range of a few GHz around the frequency of the $J=26\leftarrow 25$ line deduced from the rotational constant of Qian *et al.*[15] ($f\approx 199\,530$ MHz). After several unsuccessful attempts, a line was observed at 201 560.541 MHz when the cell was cooled to liquid nitrogen temperature. The identification of this line was confirmed by the observation of many other transitions for different J values: 25 lines were measured between 178 GHz and 473 GHz corresponding to J between 22 and 60. The rotational frequencies observed are given in Table V. A

TABLE III. Geometries (R and r), dipole moment (μ), rotational constants (B), vibration-rotation interaction constants (α), centrifugal distorsion constants (D and H), and rotational l-type doubling constants (q) for $\widetilde{X}^I\Sigma^+$ of $^{31}P_2{}^{16}O$.

Parameter	cc-pVTZ CCSD(T)	Experiment This work	Experiment Ref. 37
R_e (PP) (Å)	1.9044		
r_e (PO) (Å)	1.4806		
μ (debye)	1.67		
B_e (MHz)	3846.04	3917.9729(57)[a]	
B_0 (MHz)	3837.34	3907.669 25(18)	3907.62(17)
α_1 (MHz)	11.21	12.6651(28)	
α_2 (MHz)	-4.75	$-5.2211(49)$[b]	$-5.27(43)$[c]
α_3 (MHz)	15.43	18.5060(41)	17.37(3)[c]
D_J (kHz)	0.557	0.578 73(27)[d]	0.598(65)[e]
H_J (Hz)	-0.42×10^{-4}		
$q^e_{01^10}$ (MHz)	5.278	5.625 95(54)	5.86(16)
$q^J_{01^10}$ (Hz)	5.78	6.711(99)	
$q^K_{01^10}$ (Hz)	5.42		

[a] This value corresponds to $B_e+\gamma_{ll}$.
[b] This value corresponds to $\alpha_2+2\gamma_{ll}$.
[c] These values were deduced from a first order expansion of B_ν.
[d] Equilibrium value (see the text).
[e] This is the ground state value.

TABLE IV. Harmonic vibrational frequencies, vibrational anharmonicity constants, and certain vibrational levels of P_2O (all in units of cm^{-1}).

	cc-pVTZ CCSD(T)	Experiment[a]
ω_1	658.32	
ω_2	211.48	
ω_3	1295.69	
x_{11}	−1.94	
x_{12}	−0.75	
x_{13}	−2.82	
x_{22}	−0.31	
x_{23}	−2.84	−2.746(1)
x_{33}	−1.94	
x_{ll}	0.33	
$(100)\leftarrow(000)=\nu_1$	652.35	
$(01^10)\leftarrow(000)=\nu_2$	209.08	
$(001)\leftarrow(000)=\nu_3$	1278.80	1277.6454(3)
$(01^11)\leftarrow(01^10)$	1275.96	1274.899(1)
$(200)\leftarrow(000)$	1300.82	

[a] Reference 37.

least-squares fit of the measured lines to the following well known formula applicable for linear molecules in their ground vibrational state:

$$f=2B_{\mathrm{eff}}(J+1)-4D_{\mathrm{eff}}(J+1)^3, \tag{1}$$

led to the determination of the two structural constants: $B_{\mathrm{eff}}=3876.993\,33(18)$ MHz and $D_{\mathrm{eff}}=0.612\,786(32)$ kHz. This B value did not agree with that of Qian *et al.*[15] However, a shift of their J values by $+2$ and -2 for the $R(J)$ and $P(J)$ transitions, respectively, led to a much closer B value, $B_{\mathrm{IR}}=3872.79$ MHz. Nevertheless, it was impossible to fit both spectra together within the experimental uncertainties.

TABLE V. Rotational frequencies of P_2O in the (10^01) vibrationally excited state[a] (in MHz).

J	f	Δf[b]
22	178 311.869	−0.001
23	186 061.755	−0.040
24	193 811.338	−0.029
25	201 560.541	−0.031
27	217 057.795	−0.024
32	255 793.462	−0.011
33	263 539.206	−0.000
34	271 284.439	−0.001
35	279 029.170	0.011
44	348 706.023	−0.016
45	356 444.827	0.025
46	364 182.921	0.033
47	371 920.284	0.001
48	379 657.001	0.030
49	387 392.952	0.012
50	395 128.218	0.045
51	402 862.668	0.012
53	418 329.341	0.029
54	426 061.492	0.035
55	433 792.792	−0.001
56	441 523.278	−0.027
57	449 252.944	−0.035
58	456 981.787	−0.012
59	464 709.740	−0.012
60	472 436.785	−0.038

[a] This state was first wrongly assigned to the vibrational ground state of P_2O.

[b] $\Delta f=f_{\mathrm{obs}}-f_{\mathrm{calc}}$.

In order to resolve this discrepancy, a very careful scan in a wider frequency range was carried out around the $J=47\leftarrow46$ line. In this frequency region, a powerful BWO was used to improve sensitivity. Numerous lines have been detected when P_4 was mixed with molecular oxygen without cooling the cell. The influence of partial pressures and flow rate has been checked carefully. Finally, 19 lines, including the previously observed one, were attributed to P_2O. A prediction of the 19 corresponding frequencies for other J values was made and the same groups of lines were indeed measured. These observations confirmed that these lines belonged to a linear molecule. The related line frequencies for the various J values were then least squares fitted according to Eq. (1), resulting in a set of 19 $\{B_{\mathrm{eff}}, D_{\mathrm{eff}}\}$ effective constants. The B_{eff} values are listed in the first column of Table VI. The centrifugal distortion parameter D_{eff} are not reported as they proved to be relatively constant, as it should be for different vibrational states of a linear molecule.[54] Owing to the poor signal-to-noise ratio of most of the lines observed and to the critical dependence of the observations on the experimental conditions, line intensities could not be used as pertinent information for the assignment of the spectrum. Furthermore, due to the large exothermicity of the oxidation of white phosphorus (130 ± 10 kcal mol^{-1}),[10] observation of highly excited vibrational states is likely, and the relative intensities of the rotational transitions in different vibrational states depend on the complex global vibrational relaxation mechanism.

V. SPECTROSCOPIC ANALYSIS

Comparison of the set of B_{eff} and D_{eff} values reported in Tables VI and VII with those deduced from the infrared measurements[15,37] showed a nice coincidence between the sets (B_3, D_3) and (B_{10}, D_{10}) and the infrared values of the molecular constants in the ground and the ν_3 excited states, respectively:

$$B_{00^00}=3907.62(17)\ \ \mathrm{MHz}\qquad D_{00^00}=0.0598(65)\ \ \mathrm{kHz},$$

and

$$B_{00^01}=3890.25(17)\ \ \mathrm{MHz}\qquad D_{00^01}=0.0623(67)\ \ \mathrm{kHz}.$$

In order to proceed further with the identification of the spectrum, it proved to be essential to resort to high-quality *ab initio* structural results obtained in this study. The vibrational dependence of the rotational constant B_ν is given by

$$B_\nu=B_e-\sum_{i=1}^{3}\alpha_i\left(\nu_i+\frac{d_i}{2}\right)+\sum_{\substack{i,j=1\\ i\leqslant j}}^{3}\gamma_{ij}\left(\nu_i+\frac{d_i}{2}\right)\left(\nu_j+\frac{d_j}{2}\right)+\gamma_{ll}l^2 \tag{2}$$

while that of the centrifugal distortion constant by

$$D_\nu=D_e-\sum_{i=1}^{3}\beta_i\left(\nu_i+\frac{d_i}{2}\right). \tag{3}$$

TABLE VI. Comparison between the different sets of B_{eff} (MHz): experimental, calculated with the *ab initio* values of α_i, and calculated with the α_i deduced from the first order analysis of the rotation-vibration interaction.

Experimental		Calculated (*ab initio* α_i)		Calculated (experimental α_i)	
Level	B_{eff}	Level	B_{eff}	Level	B_{eff}
	3918.0083	02^00	3919.280	02^00	3918.0428
	3915.670 21	$01^{1f}0$	3915.058	$01^{1f}0$	3915.670 21
	3910.044 26	$01^{1e}0$	3909.780	$01^{1e}0$	3910.044 26
00^00	3907.669 25	00^00	3907.66925	00^00	3907.669 25
	3903.635 67	$11^{1f}0$	3903.848	$11^{1f}0$	3903.7196
	3898.418 32	$01^{1f}1$	3899.628	$01^{1f}1$	3898.2820
	3897.994 78	$11^{1e}0$	3898.570	$11^{1e}0$	3898.0788
	3895.712 46	10^00	3896.459	10^00	3895.712 46
	3893.027 91	$01^{1e}1$	3894.350	$01^{1e}1$	3892.6412
	3892.777 19	$21^{1f}0$	3892.638	$21^{1f}0$	3891.7629
00^01	3890.274 85	00^01	3892.239	00^01	3890.274 85
	3887.371 25	$11^{1f}1$	3888.418	$11^{1f}1$	3886.3252
	3886.3057	$21^{1e}0$	3887.360	$21^{1e}0$	3886.1221
	3885.211 57	20^00	3885.249	20^00	3883.7557
	3882.3004	$01^{1f}2$	3884.198	$01^{1f}2$	3880.8876
	3880.6909	$11^{1e}1$	3883.140	$11^{1e}1$	3880.6844
	3876.993 33	10^01	3881.029	10^01	3878.3181
	3876.625 43	$01^{1e}2$	3878.920	$01^{1e}2$	3875.2468
	3874.519 50	00^02	3876.809	00^02	3872.8805
		30^00	3874.039	30^00	3871.7989

In these expressions, the factors α_i, β_i, γ_{ij}, and γ_{ll} are vibration-rotation interaction constants, l is the total vibrational angular momentum along the molecular axis, and d_i is the degeneracy of the ith vibrational mode.[54] The expansion is truncated after the second-order term in Eq. (2) and after the first-order term in Eq. (3).

If Eq. (2) is truncated after the first order term, B_ν can be written as

$$B_\nu = B_{00^00} - \alpha_1 \nu_1 - \alpha_2 \nu_2 - \alpha_3 \nu_3 . \tag{4}$$

The *ab initio* values of the first-order vibration-rotation interaction terms α_i given in Table III were used together

TABLE VII. Effective and true molecular constants for the observed vibrational levels of P_2O.

Level	B_{eff}(MHz)	D_{eff}(kHz)	B_ν(MHz)	D_ν(kHz)	q_ν(MHz)	q_ν^J(Hz)
02^20	3918.0083(15)	0.613 20(23)	3918.0034(15)	0.613 20(23)		
	3915.6702(27)	0.607 533(51)				
01^10			3912.856 03(27)	0.604 178(50)	5.625 95(54)	6.711(99)
	3910.044 26(27)	0.600 822(48)				
00^00	3907.669 25(18)	0.595 230(31)	3907.669 25(18)	0.595 230(31)		
	3903.635 67(56)	0.610 988(87)				
11^10			3900.814 02(36)	0.607 660(55)	5.640 89(71)	6.66(11)
	3897.994 78(15)	0.604 332(23)				
10^00	3895.712 46(19)	0.598 810(33)	3895.712 46(19)	0.598 810(33)		
	3898.418 32(52)	0.619 005(84)				
01^11			3895.596 52(51)	0.615 760(81)	5.6411(10)	6.49(16)
	3892.777 19(50)	0.612 515(77)				
00^01	3890.274 85(35)	0.606 747(60)	3890.274 85(35)	0.606 747(60)		
	3893.027 91(94)	0.601 07(14)				
21^10			3890.198 38(77)	0.597 66(12)	5.6567(15)	6.83(11)
	3887.371 25(60)	0.594 240(91)				
20^00	3885.211 57(39)	0.588 796(60)	3885.211 57(39)	0.588 796(60)		
	3886.3057					
11^11[a]			3883.5785	0.6217	5.6583	6.7[b]
	3880.6909					
	3882.3004(35)	0.602 02(54)				
01^12			3879.4617(22)	0.598 37(34)	5.6750(13)	7.300(68)
	3876.625 43(94)	0.594 72(14)				
10^01	3876.993 33(18)	0.612 786(32)	3876.993 33(18)	0.612 786(32)		
00^02	3874.519 50(92)	0.589 50(14)	3874.519 50(92)	0.589 50(14)		

[a] Only one transition was measured for this level. We used $D_{11^11} = D_{10^01} - \beta_2$ (see the text).
[b] Fixed to the mean value of the various q_ν^J values.

with the experimental B_{00^00} to calculate the B_ν constants of the lowest vibrationally excited states. For the nondegenerate vibrational levels, $B_{\mathrm{eff}}=B_\nu$. However, for a linear triatomic molecule, the bending mode is doubly degenerate. In P_2O, it is predicted to lie at 209 cm^{-1} (Table IV) and could be easily populated due to the exothermicity of the oxidation of phosphorus. In this degenerate mode and for $l\neq 0$, each transition is split into e and f components by l-type doubling. Both components can be fitted to the effective parameters of Eq. (1). For the Π states, their frequencies are given by

$$f^{f,e}=2(B_\nu+2D_\nu l^2\pm 1/2q_\nu)(J+1)$$
$$-4(D_\nu\pm 1/2q_\nu^J)(J+1)^3, \tag{5}$$

where q_ν denotes the l-type doubling constant and q_ν^J its centrifugal distortion correction term. The correspondence between the effective parameters in (1) and the molecular parameters in (5) is clear. The l-type doubling constants q_{01^10} and $q_{01^10}^J$ were calculated *ab initio* (see Table III) and were used to determine the various B_ν constants. The complete list of the calculated effective rotational constants is given in the fourth column of Table VI together with the corresponding vibrational state identification (third column). They should be compared with the measured values given in the second column of this table. Identification of the fundamental vibrational levels (01^10) and (10^00) was obvious. This led, together with the knowledge of the (00^01) level, the ground state, and the first order expansion of B_ν [see Eq. (4)], to an approximate determination of α_1, α_2, and α_3, as follows

$$\alpha_1=11.956\,79(37)\ \ \mathrm{MHz},\quad \alpha_2=-5.186\,78(45)\ \ \mathrm{MHz},$$

and

$$\alpha_3=17.394\,40(53)\ \ \mathrm{MHz}.$$

These values were then used for a more precise prediction of the effective rotational constants of the various vibrational states. The results obtained are given in the sixth column of Table VI. Comparison with the experimental values led to a provisional identification of the observed vibrational levels as given in the first column of Table VII. This completes the first phase of our spectroscopic analysis.

The measured frequencies for the ground and various vibrational states excited by one, two, or three quanta are given in Tables VIII, IX, X, and XI, respectively.

For the tentatively assigned (11^11) level, the very poor signal-to-noise ratio allowed the observation of the two components of only the $J=56$ transition:

$$f^f=442\,587.573\ \ \mathrm{MHz}$$

$$f^e=441\,947.485\ \ \mathrm{MHz}.$$

Identification proved to be relatively easy for most vibrationally excited states and was also supported for the Π levels by the value of q_ν which had to remain nearly constant (see Table VII). Nevertheless, a few problems remained.

TABLE VIII. Rotational frequencies of P_2O in the vibrational ground state (in MHz).

J	f	Δf[a]
24	195 346.240	−0.021
25	203 156.900	−0.054
42	335 870.268	0.012
43	343 672.097	0.019
44	351 473.290	0.019
45	359 273.822	0.000
46	367 073.719	0.004
47	374 872.955	0.018
48	382 671.483	0.009
49	390 469.313	0.003
50	398 266.443	0.011
51	406 062.829	0.003
52	413 858.471	−0.005
53	421 653.366	−0.004
54	429 447.493	0.001
55	437 240.832	0.003
56	445 033.346	−0.019
57	452 825.075	−0.012
58	460 615.982	0.001
59	468 406.020	−0.012

[a] $\Delta f=f_{\mathrm{obs}}-f_{\mathrm{calc}}$

The first difficulty concerned the choice between (00^02) and (30^00), as well as between (01^12) and (31^10), which was not obvious when based on the predicted and experimental parameters of Table VI. We chose the labels (00^02) and (01^12) based on the argument that they contain less quanta. This identification will be checked later in this article.

The second difficulty is related to the identification of the l-component observed for the $2\nu_2$ level, while the third one to the confirmation of the (11^11) state.

For a nondegenerate level, $B_\nu=B_{\mathrm{eff}}$ and $D_\nu=D_{\mathrm{eff}}$. For the Π states, the true molecular constants can be derived from the effective parameters as follows:

$$q_\nu=B_{\mathrm{eff}}^f-B_{\mathrm{eff}}^e \tag{6}$$

$$q_\nu^J=D_{\mathrm{eff}}^f-D_{\mathrm{eff}}^e \tag{7}$$

$$D_\nu=D_{\mathrm{eff}}^{f/e}\mp\tfrac{1}{2}\,q_\nu^J \tag{8}$$

and

$$B_\nu=B_{\mathrm{eff}}^{f/e}\mp\tfrac{1}{2}\,q_\nu-2D_\nu. \tag{9}$$

For the Σ and Δ, $\nu_2=2$ states, the transition frequencies are given by[55]

$$f_{l=0}=2\left(B_{02^00}+2\,\frac{q_{02^00}^2}{\delta}\right)(J+1)$$
$$-4\left(D_{02^00}+\frac{q_{02^00}^2}{\delta}\right)(J+1)^3 \tag{10}$$

$$f_{l=2}^f=2\left(B_{02^20}+8D_{02^20}-2\,\frac{q_{02^20}^2}{\delta}\right)(J+1)$$
$$-4\left(D_{02^20}-\frac{q_{02^20}^2}{\delta}\right)(J+1)^3 \tag{11}$$

and

TABLE IX. Rotational frequencies of P_2O in vibrational states excited by one quantum (in MHz).

	$(10^{0}0)$		$(01^{1e}0)$		$(01^{1f}0)$		$(00^{0}1)$	
J	f	Δf[a]	f	Δf[a]	f	Δf[a]	f	Δf[a]
23	186 961.099	0.013						
24	194 748.193	−0.005	195 464.651	−0.011	195 745.509	−0.031	194 475.756	−0.065
25	202 534.908	−0.041	203 280.036	−0.026	203 572.143	0.004	202 251.566	−0.069
43	342 618.664	0.003					342 137.456	0.010
44			351 685.077	0.093	352 188.850	−0.023		
45	358 172.395	−0.009	359 490.144	−0.002	360 005.157	0.037	357 669.088	0.035
46	365 948.291	0.000	367 294.730	0.086	367 820.694	−0.002	365 433.861	0.002
47	373 723.527	0.025	375 098.455	−0.010	375 635.571	−0.016	373 198.004	0.024
48	381 498.028	0.004	382 901.609	0.016	383 449.803	0.025	380 961.404	0.001
49			390 704.029	0.014	391 263.270	0.016	388 724.120	0.009
50			398 505.735	0.019	399 076.008	0.006	396 486.116	0.024
51	404 817.310	0.004	406 306.710	0.028	406 888.011	0.005	404 247.358	0.028
53	420 359.799	0.017					419 767.549	0.028
54	428 129.866	0.003	429 705.025	0.003	430 319.384	−0.026	427 526.463	0.020
55	435 899.175	0.021	437 502.916	0.014	438 128.311	0.018	435 284.593	0.028
56	443 667.639	−0.000	445 299.941	−0.033	445 936.364	0.004	443 041.872	0.000
57	451 435.264	−0.042	453 096.198	−0.026	453 743.571	−0.025	450 798.332	−0.016
58	459 202.155	0.016					458 553.953	−0.027
59	466 968.119	−0.005					466 308.715	−0.038
60	474 733.231	−0.016					474 062.612	−0.040

[a] $\Delta f = f_{\mathrm{obs}} - f_{\mathrm{calc.}}$

$$f^{e}_{l=2} = 2(B_{02^20} + 8D_{02^20})(J+1) - 4D_{02^20}(J+1)^3, \quad (12)$$

where $\delta = E^0_\Delta - E^0_\Sigma$ is the difference between the unperturbed energies of the Δ and Σ states.

It is clear from these formulas that only the e component of the $l=2$ level gives an effective distortion parameter similar to that of the other vibrational states. This has clearly been observed in the case of N_2O[34] and HCN.[55]

The term q^2_ν/δ was estimated with the help of the *ab initio* calculated vibrational anharmonicity constant x_{ll} (Table IV):

$$\delta = 4x_{ll} + 4\gamma_{ll}[J(J+1) - 1] - 4B_{02^00}. \quad (13)$$

Neglecting the term in γ_{ll} and using an approximate value of $B_{02^00} = 2B_{01^10} - B_{00^00}$ and the *ab initio* value of x_{ll} we obtained

TABLE X. Rotational frequencies of P_2O in vibrational states excited by two quanta (in MHz).

	$(11^{1e}0)$		$(11^{1f}0)$		$(01^{1e}1)$		$(01^{1f}1)$	
J	f	Δf[a]	f	Δf[a]	f	Δf[a]	f	Δf[a]
24	194 861.976	0.008	195 143.538	−0.059			194 882.219	−0.009
25	202 653.240	−0.001	202 946.138	0.038			202 674.220	−0.014
53	420 602.776	−0.018	421 207.836	0.018	420 034.136	−0.005	420 639.323	0.028
54	428 377.250	0.008	428 993.340	0.029	427 797.859	−0.004	428 414.080	0.012
55	436 150.886	−0.007	436 778.022	0.024	435 560.791	0.015	436 188.033	0.009
56	443 923.732	−0.000	444 561.841	−0.023	443 322.868	0.002	443 961.180	0.033
57	451 695.752	0.008	452 344.888	−0.005	451 084.108	−0.010	451 733.416	−0.008
58	459 466.916	0.001	460 127.041	−0.032			459 504.781	−0.059
59	467 237.235	0.005	467 908.387	0.000	466 604.052	0.002		

	$(20^{0}0)$		$(02^{2e}0)$		$(00^{0}2)$	
J	f	Δf[a]	f	Δf[a]	f	Δf[a]
25	201 989.619	0.012				
53	419 231.964	−0.029	422 758.677	0.004	418 076.781	−0.023
54	426 981.439	0.010	430 572.823	−0.010	425 804.832	0.002
55	434 730.092	0.004	438 386.214	0.031	433 532.092	0.013
56	442 477.948	−0.008	446 198.681	−0.029	441 258.549	0.014
57	450 225.003	−0.015	454 010.382	−0.015	448 984.208	0.023
58	457 971.281	0.021	461 821.249	0.018	456 708.995	−0.020
59	465 716.680	0.011			464 433.000	−0.009

[a] $\Delta f = f_{\mathrm{obs}} - f_{\mathrm{calc}}$.

TABLE XI. Rotational frequencies of P_2O in vibrational states excited by three quanta (MHz).

	$(21^{1e}0)$		$(21^{1f}0)$		$(01^{1e}2)$		$(01^{1f}2)$	
J	f	Δf[a]	f	Δf[a]	f	Δf[a]	f	Δf[a]
53			420 068.435	0.008	418 300.952	−0.007		
54	427 215.375	0.004	427 833.038	−0.020			426 652.398	−0.003
55	434 968.145	−0.003	435 596.923	0.027	433 764.292	0.013	434 394.738	−0.011
56	442 720.126	0.000	443 359.921	−0.005	441 494.762	0.014	442 136.336	0.049
57	450 471.282	−0.009	451 122.127	−0.007	449 224.385	−0.018	449 876.948	−0.055
58	458 221.637	0.007	458 883.486	−0.019	456 953.212	−0.017	457 616.899	0.019
59			466 644.043	0.018	464 681.229	0.015		

[a] $\Delta f = f_{\text{obs}} - f_{\text{calc}}$

$$\delta \cong 23\,900 \text{ MHz}.$$

and

$$\frac{q_\nu^2}{\delta} \cong 1.3 \text{ kHz using } \quad q_{020} \cong q_{01^10}.$$

This value which is twice as large as the true D_ν values, induces a large variation in the D_{eff} value for the $l=0$ and $l=2$, f components.

This observation led us to the conclusion that the $2\nu_2$ lines that we observed correspond to the $l=2$, e component. The two other components were not observed due to a very poor signal-to-noise ratio.

The true B_ν and D_ν constants have been deduced from Eq. (12):

$$D_{02^20} = D_{\text{eff}} \tag{14}$$

and

$$B_{02^20} = B_{\text{eff}} - 8D_{\text{eff}}. \tag{15}$$

The complete list of the molecular parameters determined is given in Table VII.

The β_i and D_e constants were deduced according to Eq. (3) from D_{00^00}, D_{01^10}, D_{10^00}, and D_{00^01}. These parameters are given in Table XII. The D_ν parameter is very sensitive to anharmonic resonances[57] and it probably explains why the experimental values D_{n0^0m} are not in closer agreement with the values calculated using Eq. (3). Nevertheless, the D_{n1^1m} are well predicted with the formula deduced from Eq. (3)

$$D_{n1^1m} = D_{n0^0m} - \beta_2 \tag{16}$$

The calculated values of $D_{02^20} = 2D_{01^10} - D_{00^00} = 0.613\,13(13)$ kHz strongly supports our identification of the (02^20) level for which the measured distortion constant is 0.613 20(23) kHz.

In order to confirm the assignment of Table VII for the 13 vibrational states, the equilibrium rotational constant B_e and the rovibrational interaction constants α_i, γ_{ij}, and γ_{ll} [see Eq. (2)] have been determined.

Since no transition was measured in the $2\nu_2$, Σ level, the γ_{ll} parameter could not be determined. This parameter is expected to be very small, based on its value in N_2O,[34] HCN,[55] and OCS.[56] Therefore, the combinations $\gamma_{22} + \gamma_{ll}$, $\alpha_2 + 2\gamma_{ll}$, and $B_e + \gamma_{ll}$ have been determined instead of γ_{22}, α_2, γ_{ll}, and B_e. The 10 parameters were deduced from the molecular constants of 10 vibrational levels: the (21^10), (01^12), and (11^11) levels were not taken into account but their rotational and centrifugal distortion constants were compared to the calculated values deduced from Eqs. (2) and (16). They have been used to check the consistency of our analysis. Each parameter was expressed in terms of B_ν combinations and the uncertainty was deduced from the standard deviations of the various B_ν values. These constants are listed in Table XII.

In Table XIII, the calculated rotational and centrifugal distortion constants for the (21^10), (01^12), and (11^11) levels are compared with their experimental counterparts. As the lines observed in the (11^11) vibrational level correspond to a single J value, the centrifugal distortion parameter was fixed to the value deduced from Eq. (16):

$$D_{11^11}^{\text{calc}} = D_{10^01} - \beta_2 = 0.621\,73(11) \text{ kHz}$$

and B_{11^11} was then deduced from Eq. (5).

For the (21^10) and (01^12) vibrational levels, the experimental D_ν values are in excellent agreement with the calculated ones, the errors are well within the respective standard deviations. The experimental B_ν values are also in good agreement, even if the difference is larger for the (01^12) level, 514 kHz.

As far as the (11^11) level is concerned, the difference between the experimental and the calculated rotational con-

TABLE XII. Equilibrium rotational and centrifugal distortion constants expansion.

$B_e + \gamma_{ll}$ (MHz)	3917.9729(57)
α_1 (MHz)	12.6651(28)
$\alpha_2 + 2\gamma_{ll}$ (MHz)	−5.2211(49)
α_3 (MHz)	18.5060(41)
γ_{11} (MHz)	0.727 95(48)
γ_{12} (MHz)	−0.085 22(99)
γ_{13} (MHz)	−1.324 73(90)
$\gamma_{22} + \gamma_{ll}$ (MHz)	−0.0197(11)
γ_{23} (MHz)	0.1349(13)
γ_{33} (MHz)	0.819 53(90)
D_e (kHz)	0.578 73(27)
β_1 (Hz)	−3.580(64)
β_2 (Hz)	−8.948(81)
β_3 (Hz)	−11.517(91)
q_1 (kHz)	−14.94(125)
q_3 (kHz)	−15.15(154)

TABLE XIII. Comparison between experimental and calculated molecular parameters for the (21^10), (01^12), and (11^11) vibrational levels.

Constants	Experimental value	Calculated value
B_{21^10} (MHz)	3890.198 38(77)	3890.2279(19)
D_{21^10} (kHz)	0.597 66(12)	0.597 74(14)
B_{01^12} (MHz)	3879.4617(22)	3879.9761(31)
D_{01^12} (kHz)	0.598 37(34)	0.598 45(22)
B_{11^11} (MHz)	3883.5785	3882.2298(20)
q_{11^11} (MHz)	5.6583	5.6560(23)

stant is relatively large, 1.349 MHz. Nevertheless, the experimental B_ν value could be easily adjusted to the calculated value by changing the calculated centrifugal distortion constant by only 1 Hz. Moreover, the first-order expansion of the l-doubling constant q_ν:[34,56]

$$q_\nu = q_e - \sum_{i=1}^{3} q_i\left(\nu_i + \frac{d_i}{2}\right) \tag{17}$$

leads to $q_{\nu_1\nu_2\nu_3} = q_{01^10} - q_1\nu_1 - q_2(\nu_2 - 1) - q_3\nu_3$ (18)

and to $q_{11^11} = q_{11^10} + q_{01^11} - q_{01^10}$. (19)

The calculated value $q_{11^11} = 5.6560(23)$ MHz agrees very well with the experimental value, 5.6583 MHz (Table XIII), and contributes to the confirmation of the identification. The experimental coefficients q_1 and q_3 are given in Table XII.

In order to confirm the identification of the (00^02) vibrational state, the rovibrational interaction constants were used to calculate B_{30^00}:

$$B_{30^00}^{\mathrm{calc}} = 3876.1666(75)\ \ \mathrm{MHz}.$$

This value is 1.6471 MHz larger than the experimental value, which seems to corroborate our identification. For the (31^10) level, the calculated B_ν value is 1.6361 MHz larger than the experimental value which also tends to confirm our identification of the (01^12) level.

The discrepancies between some experimental centrifugal distortion constants and the calculated values obtained using expansion (3) show that there are probably some anharmonic resonances, which can also explain the discrepancies between the calculated and experimental values of the rotational constants. The *ab initio* calculated energies of the vibrational levels in Table IV show that a Fermi resonance can occur between $2\nu_1$ and ν_3 even if it should be relatively weak due to the small value of the cubic force constant ϕ_{113} (Table II).

VI. FIRST-ORDER ANHARMONIC RESONANCE

In the case of a Fermi resonance between $2\nu_1$ and ν_3, the off-diagonal matrix element coupling the vibrational levels in the Hamiltonian is given by[56]

$$\langle \nu_1\nu_2^l\nu_3 || \nu_1 - 2, \nu_2^l, \nu_3 + 1\rangle = \tfrac{1}{4}\phi_{113}\{\tfrac{1}{2}\nu_1(\nu_1 - 1)(\nu_3 + 1)\}^{1/2},$$

where ϕ_{113} is the cubic force constant in normal coordinates (see Table II). In this expression, we have neglected the ν and J dependence of the force constant.

Many of the observed vibrational levels listed in Table VII could be perturbed by such a resonance but only two pairs of interacting levels have been observed: (20^00)-(00^01) and (21^10)-(01^11). We analyzed the resonance for these two pairs of levels using a least squares procedure through the diagonalization of the Hamiltonian. It led to the determination of unperturbed molecular parameters, of the energy difference between the two interacting levels and of the cubic force constant ϕ_{113}. These parameters are given in Table XIV.

The B rotational constants are modified by less than 1.5 MHz. Nevertheless, these variations may affect considerably the second-order rovibrational interaction parameters. As we did not observe enough vibrational levels to correct all the rotational constants which were used to calculate the αs and γs, we were not able to determine the true unperturbed B_e parameter.

For the two pairs of levels which have been analyzed, the vibrational energy differences ΔE are roughly constant, 23.6 cm^{-1}, and close to the *ab initio* value, 22.1 cm^{-1}. The experimental value of ϕ_{113}, 55.8 cm^{-1}, differs by 20% from the value calculated *ab initio*, 45.7 cm^{-1}.

VII. CONCLUSION

Synthesis of P_2O by the chemiluminescent reaction of atomic or molecular oxygen with the vapor of white phosphorus led to the detection of the millimeter-wave spectrum of this compound. The exothermicity of the oxidation reaction allowed observation of 13 vibrational states. Identifica-

TABLE XIV. Unperturbed molecular constants in the (20^00), (00^01), (21^10), and (01^11) vibrational levels. Energy differences and cubic force constants.

	(20^00)	(00^01)	(21^10)	(01^11)
B (MHz)	3883.833 37(26)	3891.652 28(20)	3888.718 86(65)	3897.077 74(63)
D (kHz)	0.572 817(45)	0.622 613(35)	0.609 13(11)	0.604 53(15)
q_ν (MHz)			5.6365(13)	5.6605(13)
q_ν^J (Hz)			4.55(18)	8.67(20)
ΔE (cm^{-1})	23.6613(25)		23.5498(51)	
ϕ_{113} (cm^{-1})	55.7604(52)		55.899(13)	

tion of the lines detected was partially based on high level *ab initio* structural results. The equilibrium rotational constants B_e and D_e, and the rovibrational interaction constants α_i, γ_{ij}, and β_i, were deduced from the various effective B_v and D_v parameters. The weak Fermi resonance between $2\nu_1$ and ν_3 was confirmed and analyzed. High vibrational excitation was observed for both stretching modes (ν_1 and ν_3) but not for the bending mode ν_2. This is probably due to a fast thermalization of the ν_2 manifold, the various levels being close in energy.

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