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A dispersed fluorescence and *ab initio* investigation of the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$ electronic states of the PH_2 molecule

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In this work, the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$ electronic states of the phosphino (PH_2) free radical have been studied by dispersed fluorescence and *ab initio* methods. PH_2 molecules were produced in a molecular free-jet apparatus by laser vaporizing a silicon rod in the presence of phosphine (PH_3) gas diluted in helium. The laser-induced fluorescence, from the excited $\tilde{A}\,^2A_1$ electronic state down to the ground electronic state, was dispersed and analyzed. Ten ($v_1v_2v_3$) vibrationally excited levels of the ground electronic state, with $v_1 \leqslant 2$, $v_2 \leqslant 6$, and $v_3=0$, have been observed. *Ab initio* potential-energy surfaces for the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$ electronic states have been calculated at 210 points. These two states correlate with a $^2\Pi_u$ state at linearity and they interact by the Renner-Teller coupling and spin-orbit coupling. Using the *ab initio* potential-energy surfaces with our RENNER computer program system, the vibronic structure and relative intensities of the $\tilde{A}\,^2A_1 \rightarrow \tilde{X}\,^2B_1$ emission band system have been calculated in order to corroborate the experimental assignments. *© 2006 American Institute of Physics*. [DOI: 10.1063/1.2168155]

I. INTRODUCTION

The phosphino (PH_2) free radical is of spectroscopic and astrophysical interest. Unlike the isovalent amidogen (NH_2) free radical, which undergoes a bent to nearly linear $\tilde{A}\,^2A_1 \leftarrow \tilde{X}\,^2B_1$ transition, PH_2 is strongly bent in both states. These states, which correlate with a $^2\Pi_u$ state at linearity, have been extensively studied experimentally and theoretically. The spectrum of PH_2 was first obtained 50 years ago[1] by the flash photolysis of phosphine (PH_3). In that work Ramsay recorded a long progression of absorption bands assigned to the series $(0v_2'0)$–(000), with $v_2'=0$–10, of the $\tilde{A}\,^2A_1 \leftarrow \tilde{X}\,^2B_1$ system. Since that time the (000) level of the ground electronic state has been characterized in detail by high-resolution absorption spectroscopy,[2,3] laser magnetic-resonance spectroscopy,[4–7] microwave spectroscopy,[8–10] terahertz spectroscopy,[11] and intermodulated fluorescence spectroscopy.[12] There have been several works focused on the bending vibrations of the $\tilde{X}\,^2B_1$ state including studies by laser magnetic-resonance spectroscopy ($v_2=1$),[6] high-resolution emission spectroscopy ($v_2=1$–3),[3,13,14] and low-resolution emission spectroscopy ($v_2=0$–9).[15,16] The ν_1 fundamental has been observed by laser photoelectron spectroscopy[17,18] and high-temperature Raman spectroscopy.[19] For the ground electronic state the ν_3 fundamental, as well as higher stretching and combination vibrations, has not been observed prior to this project. The $\tilde{A}\,^2A_1$ state has been investigated by high-resolution absorption spectroscopy for the (000) level[2] and for the $v_2'=1$–8 levels,[3] as well as by low-resolution[15,16] and high-resolution[13,14] emission spectroscopy techniques. The stretching vibrations, ν_1 and ν_3, have not been observed for the $\tilde{A}\,^2A_1$ state.

The PH_2 molecule has also been the subject of several computational studies.[20–24] As in the case of the NH_2 molecule, the $\tilde{X}$ and $\tilde{A}$ states of PH_2 are subject to both the Renner-Teller interaction and spin-orbit coupling. The rovibronic energy level pattern of the states has been modeled by Alijah and Duxbury[25] who followed the approach developed previously by Barrow *et al.*[26] and Duxbury and Dixon.[27] However, prior to the present work, no *ab initio* calculation of the rovibronic term values that includes both the Renner effect and spin-orbit coupling has been attempted. In the present paper we do this following the same procedure that we used in our work on the NH_2 molecule.[28,29]

The goal of this project is to assign the fluorescence spectrum, and to characterize the vibronic structure of the $\tilde{A}$ and $\tilde{X}$ electronic states of PH_2, by experimental and *ab initio* methods.

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TABLE I. The potential-energy parameters (in cm^{-1} unless otherwise indicated) for the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$ states.

$r_{12}^{(\text{ref})}/\text{Å}$	1.386 178(29)[a]	
$a_1/\text{Å}^{-1}$	1.794 7(65)	
$f_{11}^{(0)}$	29 428(215)	
$f_{13}^{(0)}$	−2 286(35)	
$f_{111}^{(0)}$	1 564(94)	
$f_{113}^{(0)}$	−1 043(17)	
$f_{1111}^{(0)}$	2 940(31)	
$f_{1113}^{(0)}$	1 488(116)	
$f_{1133}^{(0)}$	1 808(143)	
	$\tilde{X}\,^2B_1(\sigma=-)$	$\tilde{A}\,^2A_1(\sigma=+)$
$f_0^{(1,\sigma)}$	−80 059[b](21)	−42 568(30)
$f_0^{(2,\sigma)}$	128 819(115)	121 348(233)
$f_0^{(3,\sigma)}$	−145 465(263)	−225 373(818)
$f_0^{(4,\sigma)}$	106 891(288)	279 870(1427)
$f_0^{(5,\sigma)}$	−41 711(152)	−187 027(1204)
$f_0^{(6,\sigma)}$	6 884(31)	51 721(391)
$f_1^{(1,\sigma)}$	−15 978(57)	−4 311(36)
$f_1^{(2,\sigma)}$	30 271(111)	11 646(130)
$f_1^{(3,\sigma)}$	−23 204(91)	−15 736(186)
$f_1^{(4,\sigma)}$	5 602(24)	6 095(87)
$f_{11}^{(1,\sigma)}$	−6 470(50)	−239(71)
$f_{11}^{(2,\sigma)}$	11 563(81)	3 022(157)
$f_{11}^{(3,\sigma)}$	−5 798(39)	−3 965(103)
$f_{13}^{(1,\sigma)}$	2 899(115)	3 454(205)
$f_{13}^{(2,\sigma)}$	−2 141(152)	−3 492(448)
$f_{13}^{(3,\sigma)}$	1 505(63)	2 761(289)
$f_{111}^{(1,\sigma)}$	1 189(52)	1 685(89)
$f_{111}^{(2,\sigma)}$	−477(34)	−2 302(87)
$f_{113}^{(2,\sigma)}$	924(21)	241(56)
$f_{1111}^{(1,\sigma)}$		−3 584(71)
$f_{1113}^{(1,\sigma)}$	−1 424(161)	−4 225(241)
$f_{1133}^{(1,\sigma)}$	−816(190)	−4 818(301)

[a] One standard error given in parentheses in units of the last figure quoted for the parameter.

[b] The value of $f_0^{(1,-)}$ was changed to $-80\,123\ \text{cm}^{-1}$ (see text) in the modified potential-energy function used for calculating the energies and intensities.

II. EXPERIMENT

PH_2 molecules were produced in a free-jet molecular-beam apparatus by the reaction of a silicon plasma with phosphine gas diluted in helium. A rotating and translating silicon rod was ablated, using the third harmonic (354.7 nm, 5 mJ/pulse, 10 Hz) of a Nd:YAG laser (Lumonics, YM200) focused to an approximately 1 mm^2 spot, in the presence of a helium carrier gas doped with 2%–3% of phosphine (Matheson). The reaction products, such as PH_2 and SiP,[30] seeded in helium, were expanded into vacuum through a 2-mm-diam orifice which cooled the internal degrees of freedom. The backing pressure was about 40 psi, and the background pressure in the chamber was maintained below 10^{-5} torr.

The PH_2 molecules were excited at right angles to the free-jet expansion, about 4 cm downstream from the nozzle, by an excimer-pumped (Lumonics, HyperEx-400) pulsed dye laser (Lumonics, HyperDye 300). The laser-induced fluorescence was monitored using a 1 m Spex monochromator equipped with a cryocooled photomultiplier tube (Hamamatsu, R943-02). The output signal from the photomultiplier was amplified using a 300 MHz bandwidth preamplifier (Stanford Research, SR445), integrated using a gated integrator (Stanford Research, SR250), and stored in a computer.

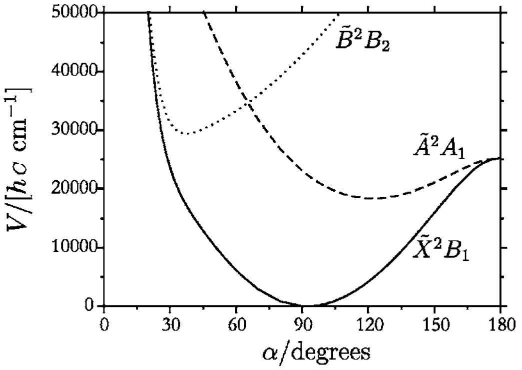

FIG. 1. The $\tilde{X}$,$\tilde{A}$, and $\tilde{B}$ CPV5Z-fc potential curves along the bending coordinate α. The stretching coordinates are fixed at $r_{12}=r_{13}=1.4$ Å.

Excitation spectra were detected by scanning the excitation laser and recording the induced fluorescence through the monochromator set at, or detuned slightly to the red of, the laser wavelength. For a satisfactory signal-to-noise ratio, 10–50 shots were averaged per point. The scanning step ranged from 0.2 cm^{-1} in the initial survey spectra to 0.03 cm^{-1} in the rotationally resolved spectra. The spectral resolution of the excitation spectra was typically 0.04–0.05 cm^{-1}. As the molecular source was rotationally cold, only transitions with $N'' \leqslant 3$ were observed.

Dispersed fluorescence spectra were recorded by pumping selected rotational levels of the $(040)\tilde{A}\,^2A_1$ excited state via the $(040)\tilde{A}\,^2A_1-(000)\tilde{X}\,^2B_1$ band, and scanning the monochromator in the vicinity, and to the red, of the excitation wavelength. The monochromator was scanned continuously at a constant rate, and the signal was averaged over 0.05–0.1 nm per point. The entrance and exit slit widths ranged from 100 to 200 μm. The experimental precision of the dispersed fluorescence spectra was estimated to be 3–5 cm^{-1}. The intensities of the dispersed fluorescence spectra were measured in several scans and averaged, without applying any further corrections. We estimate that the intensities have an experimental error that does not exceed 30% of their value.

TABLE II. Observed and calculated $N=0$ term values (T, in cm^{-1}) of the $\tilde{A}\,^2A_1$ state. In the calculation the modified potential was used (see Table I, footnote b).

	T/cm^{-1}	
$(v_1v_2v_3)$	Obs.[a]	Calc.
(000)	18 276.6	18 277
(010)	19 225.7	19 226
(020)	20 165.4	20 165
(030)	21 093.8	21 093
(040)	22 009.7	22 010
(050)	22 911.0	22 913
(060)	23 800.2	23 806

[a] Reference 3.

TABLE III. Term values (T, in cm^{-1}) of the vibrational levels of the $\tilde{X}\,^2B_1$ ground electronic state, and relative intensities (I) of the fluorescence from the (040) $\tilde{A}\,^2A_1$ level, as observed by the dispersed fluorescence spectroscopy and calculated using the modified potential surface (see Table I, footnote b).

	T			I		T
$(v_1v_2v_3)$	Obs.	Calc.	Δ	Obs.	Calc.[a]	(previous)
(000)	0	0	0	145	238	0
(010)	1102(3)	1105	−3	9	4.8	1101.9[b] 1103.5[c]
(020)	2195(3)	2197	−2	47	56	2193.5[c]
(100)	2298(3)	2309	−11	13	5	2295(15)[d] 2310(2)[e]
(001)		2314			<0.1	
(030)	3275(3)	3278	−3	32	32	3274.6[c]
(110)	3390(3)	3397	−7	5	3.1	
(011)		3398			0.3	
(040)		4347			0.3	4348[f]
(021)		4469			<0.1	
(120)		4474			0.1	
(101)		4539			<0.1	
(200)		4540			0.1	
(002)		4626			<0.1	
(050)	5404(5)	5407	−3	15	15	5407[f]
(031)		5528			<0.1	
(130)	5524(5)	5541	−17	7	3.4	
(111)		5606			<0.1	
(210)	5636(5)	5607	29	10	0.3	
(012)		5692			<0.1	
(060)	6458(5)	6457	1	8	10	6452[f]
(041)		6578			<0.1	
(140)	6586(5)	6598	−12	4	2.5	
(121)		6661			<0.1	
(220)		6663			0.2	
(300)		6685			<0.1	
(201)		6685			<0.1	
(022)		6749			<0.1	
(102)		6855			<0.1	
(003)		6858			<0.1	

[a] The calculated relative intensities were scaled so that $I(030)=32$.
[b] Reference 6.
[c] Reference 14.
[d] Reference 18.
[e] Reference 19.
[f] Reference 16.

III. COMPUTATIONAL MODELING

To further characterize the $\tilde{A}-\tilde{X}$ band system of PH_2 we have made *ab initio* calculations of the potential-energy surfaces of the $\tilde{X}$ and $\tilde{A}$ electronic states using the MOLPRO 2002 quantum chemistry package.[31,32] After fitting analytical functions through these *ab initio* energies we used the RENNER program system[28,33,34] to calculate the rovibronic energies in order to allow for the Renner-Teller coupling and spin-orbit coupling. Making use of a published *ab initio* transition moment function[35] we also calculated the relative intensities of the bands in the system. In order to account for the spin-orbit coupling we adopted a spin-orbit coupling constant A_{SO} of 200 cm^{-1} by rounding the value from Ref. 25.

The calculations were done at the CCSD(T) level; that is, we used the coupled cluster theory with all single and double substitutions from the Hartree-Fock reference determinant[36] augmented by a perturbative treatment of connected triple excitations.[37,38] We used the correlation-consistent polarized valence basis set cc-pV5Z developed by Dunning[39] and Woon and Dunning[40,41] in the frozen-core approximation. We denote this approach as CPV5Z-fc. The *ab initio* calculations were performed on a grid of 210 geometries involving bond angles from 50° to 180°, and bond lengths from 1.2 to 1.8 Å; the grids were denser in the vicinity of the $\tilde{X}$ and $\tilde{A}$ state equilibrium configurations, and the points covered energies up to 8000 cm^{-1} above equilibrium for each state. C_{2v} and C_s point-group symmetries were used to classify the electronic wave functions. We used very tight threshold values for MOLPRO2002 in order to ensure high computational precision.[42]

Using the analytical expressions for the potential surfaces given in Eqs. (8)–(11) of Ref. 28, we made a least-squares fitting to our points by adjusting the values of the parameters in the potential functions. The optimized values of the parameters are listed in Table I; the standard deviation of the fitting was 7 cm^{-1}. The parameters give the $\tilde{X}$ state equilibrium geometry at the CPV5Z-fc level as $r_e=1.4183$ Å and $\alpha_e=91.81°$, and the $\tilde{A}$ state equilibrium geometry as $r_e=1.3939$ Å and $\alpha_e=121.68°$. The height of the barrier to linearity is obtained as 24 850 cm^{-1} for the $\tilde{X}$ state and as 6686 cm^{-1} for the $\tilde{A}$ state. Figure 1 shows the potential curves along the bending coordinate direction. The figure shows that at energies that are too high to be important here there is a conical intersection of the $\tilde{A}$ state with the $\tilde{B}$ state.

IV. RESULTS AND DISCUSSION

Using transitions in the $(040)\tilde{A}\,^2A_1-(000)\tilde{X}\,^2B_1$ band, PH_2 molecules were pumped into (040) levels having $N'=0$ and 1. By recording a dispersed fluorescence from these levels ten vibrationally excited $(v_1v_2v_3)$ levels of the $\tilde{X}\,^2B_1$ ground electronic state below 7000 cm^{-1} were observed (see Table III and Fig. 2). The $\tilde{X}\,^2B_1$ ground electronic state vibrational energy separations observed in this project, as well as those for the $\tilde{A}\,^2A_1$ excited state previously reported by Berthou *et al.*,[3] were accurately reproduced using the RENNER program system[28] with the *ab initio* (CPV5Z-fc) potentials. However, the $\tilde{A}$ state term values were calculated systematically 62 cm^{-1} lower than observed.[3] This indicates that the calculated barrier height for the $\tilde{X}$ state is too low by 62 cm^{-1}. This type of result is common in *ab initio* calculations on Renner molecules, and we followed our previous practice[28,43] of decreasing the $f_0^{(1,-)}$ parameter (to $-80\,123$ cm^{-1}) in order to raise the $\tilde{X}$ state barrier appropriately to compensate for the discrepancy. Redoing the RENNER calculations with the modified potential gave the results shown in Tables II and III.

The angular dependence of the electronic transition moment integral between the $\tilde{A}$ and $\tilde{X}$ states has been calculated in Ref. 35. Using this in the RENNER program system we calculated the relative emission intensities of transitions from

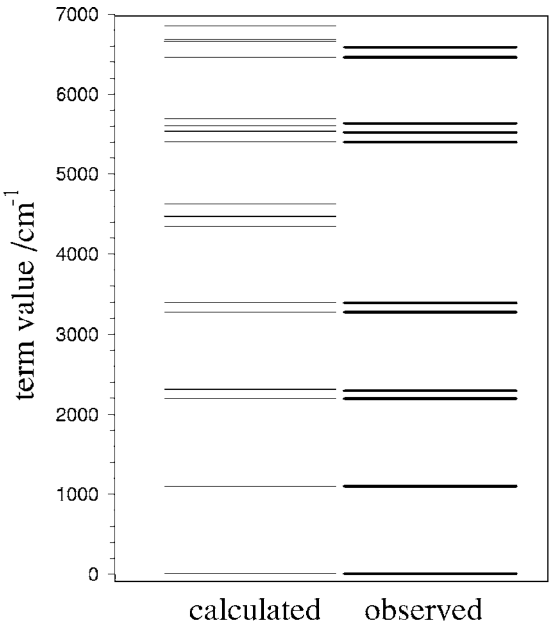

FIG. 2. Calculated and observed vibrational levels of the $\tilde{X}\,^2B_1$ ground electronic state below 7000 cm^{-1}. See Table III for labels and order of levels.

the (040) 1_{01} level of the $\tilde{A}$ state; the results are given in Table III. We have scaled our relative intensities so that the numerical value for the emission to the (030) state agrees with the intensity value given experimentally. The intensity calculation supports our assignments very well. The relative fluorescence intensities to all 19 levels predicted below 7000 cm^{-1} and not observed are calculated to be smaller than 0.3, which is significantly below our detection limit. In particular, we can satisfactorily explain the lack of observation of all six of the $2v_1+v_2+2v_3=4$ polyad levels of the $\tilde{X}$ state, particularly the (040) level, in emission from the (040) level of the $\tilde{A}$ state.

The only noticeable discrepancy between observed and calculated intensities is that for the emission to the (210) level. Coincidentally, the calculated term value of the (210) level is also in the worst agreement with experiment. The term value discrepancy may well be related to the presence of the nearby (111) level which, with $\Delta K_a = \pm 1$, has the same symmetry; in this circumstance a small change in the potential could cause a large change in the term value. However, this perturbation cannot explain the strong intensity of the fluorescence to the (210) level since the calculated intensity of fluorescence to the (111) level is very small. It should be pointed out that the dependence of the transition moment on the bond lengths was not calculated in Ref. 35. Thus our calculated relative intensities for emissions to states that involve excitation of the stretching vibrations, like the (210) and (111) levels, are not as reliable as those to the pure bending states.

As indicated above, the term values of the ground-state pure bending vibrations observed in this project generally agree very well (within experimental precision) with the computed values as well as the values obtained previously by other researchers (see Table III). Of the vibrations involving stretching modes ν_1 and ν_3 only the ν_1 fundamental was previously observed by laser photoelectron spectroscopy[17,18] and the high-temperature Raman spectroscopy.[19] Zittel and Lineberger[17] and most recently Ervin and Lineberger[18] observed an electron detachment from the PH_2^- signal attributed to the transition to the (100) level of the PH_2 ground electronic state at 2270(80) and 2295(15) cm^{-1}, respectively. Both values agree within the (somewhat large) experimental uncertainty with the value measured in this work. Abraham *et al.*[19] observed the ν_1 fundamental in the background of the Raman spectrum of PH_3. By modeling the PH_3 spectrum and subtracting it from the observed one, the PH_2 band was extracted and the term value of the (100) level determined to be 2310(2) cm^{-1}. Although this value nearly coincides with our theoretical (100) level term value, we believe that in the context of the discussion above, it is overestimated by 8–12 cm^{-1}. The calculated bending levels of the $\tilde{A}\,^2A_1$ state show excellent agreement with the observed values.

V. CONCLUSION

The rovibrational structure of the $\tilde{X}$ and $\tilde{A}$ Renner-coupled electronic states of the PH_2 molecule and the relative intensities of $\tilde{A}$–$\tilde{X}$ rovibronic transitions have been calculated *ab initio*. Experimentally, the vibrational structure of the ground state below 6600 cm^{-1} has been characterized using dispersed fluorescence spectroscopy. These theoretical and experimental studies have complemented and corroborated each other's results.

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