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Electronic Structure and Bonding in Rhodium Monophosphide

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The electronic spectrum of RhP has been detected following the reaction of laser-ablated rhodium metal with phosphine. Analysis of the observations indicates that the RhP species is strongly bound in its $^1\Sigma$ ground state, where the bond length is 0.186 nm and the $v = 1-0$ vibrational interval is 507.2 cm^{-1}.

Rhodium metal and rhodium complexes are highly regarded for their catalytic properties. One of the most famous of these complexes, Wilkinson's catalyst [$RhCl(PPh_3)_3$], is active in the hydrogenation of a wide variety of alkenes under mild conditions, where an early step in the mechanism is believed to involve rupture of an Rh−P bond with loss of one triphenylphosphine ligand. The strength of the bond depends on the substituents on phosphorus. Similar complexes, where the phosphine ligand is more strongly bound to the metal, are inactive.[1]

During the course of experiments on the reaction of a Rh plasma with PH_3, we have observed an electronic spectrum attributable to rhodium monophosphide. To our knowledge, RhP represents the first example of a transition metal monophosphide to be experimentally characterized via its electronic spectrum. Analysis of the spectrum provides insight into the participation of d electrons in the bonding. Theoretical studies of two related monophosphides, ScP and TiP, have been reported.[2,3]

The experimental conditions were similar to those used successfully to generate a spectrum of RhN.[4] A plasma of Rh atoms, created by laser vaporization of a 5 mm diameter, 99.9% purity, metal rod (Goodfellow), was allowed to react with a gas mixture of helium doped 1% with PH_3 (Sigma-Aldrich), and the products after supersonic expansion were interrogated using a Nd:YAG-pumped Lumonics HD500 tunable dye laser. At higher PH_3 concentrations, RhH[5] and PH_2[6] were detected. Three separate experiments were performed: laser-induced fluorescence (LIF) spectra were recorded between 430 and 650 nm at rotational resolution; dispersed fluorescence (DF) data were collected by fixing the wavelength of the probe laser to coincide with a strong LIF band feature and scanning the emission wavelength; and third, time decay profiles were analyzed to yield excited level lifetimes. Figure 1 shows an example of an LIF spectrum. A dispersed fluorescence scan is given in Figure 2.

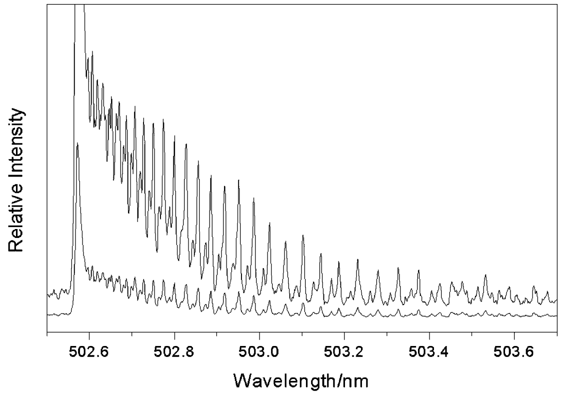

Figure 1. Laser-induced fluorescence spectrum of jet-cooled RhP near 503 nm.

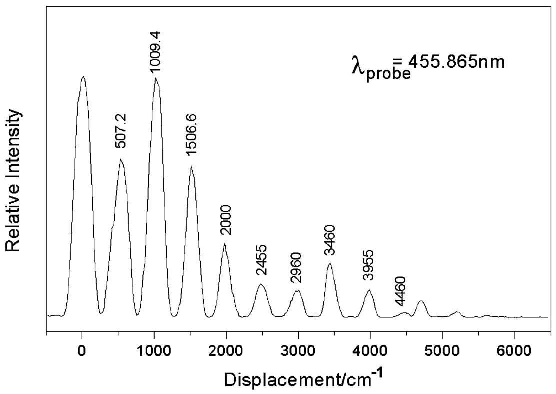

Figure 2. Dispersed fluorescence spectrum from RhP excited at 455.865 nm. The 507.2, 1009.4, and 1506.6 cm^{-1} intervals come from LIF measurements. Peaks in DF are ±15 cm^{-1}. A peak near 4700 cm^{-1} indicates a low-lying electronic state.

Although the evidence for RhP is circumstantial, the experimental observations leave little room for doubt as to the identification: (i) the spectrum does not occur when other metals are substituted for rhodium; (ii) the electronic spectrum bears the unmistakable signature of a linear molecule having a small moment of inertia; (iii) the spectrum shows nothing in common with spectra of known diatomic rhodium species, RhX, where X = H, C, N, O, F, S, Cl;[7] (iv) there is no indication of a mixture of isotopomers (both ^{103}Rh and ^{31}P occur in 100% natural abundance); and, most importantly, (v) the electronic, vibrational, and rotational characteristics of the observed species match closely expectations for RhP.

The LIF spectrum is rich in molecular features. All sixteen strong bands that have been found display a profile similar to that in Figure 1 and degrade to longer wavelengths. Two rotational branches are present, an R branch which rapidly forms the prominent head and a more open P branch. In favorable circumstances, lines of the returning R branch can be distinguished from the overlaying P structure. This general profile is typical of a vibronic transition between two $^1\Sigma$ electronic states. In most instances, there are weaker bands to lower energies of the main bands at displacements of 507.2, 1009.4, and 1506.6 cm^{-1}. That these intervals provide the energies of the $v = 1, 2,$

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TABLE 1: Observed Band Heads (λ_{air}) and Excited State Lifetimes τ in the LIF Spectrum of RhP[a]

λ/nm	int.	τ/ns	λ/nm	int.	τ/ns
431.185	s	88(2)	465.788	s	313(5)
437.326	s	110(3)	472.930	vs	267(5)
447.377	s	143(3)	482.367	s	410(5)
453.882	vs	96(2)	489.400	s	560(10)
455.864	s	105(3)	496.130	s	625(10)
459.000	s	313(5)	502.570	s	925(10)
461.237	vs	132(3)	509.298	s	780(10)
463.489	s	467(5)	540.257	s	265(5)

[a] Numbers in parentheses give estimated errors for the last quoted digit.

and 3 ground vibrational levels is confirmed by the DF data. The derived vibrational constants, $\omega_e = 512.2$ and $\omega_e x_e = 2.5$ cm^{-1}, indicate that the Rh−P bonding in the diatomic molecule is very strong. Consistent with this analysis is the observation of a short Rh−P bond.

Rotational analyses to determine ground and excited-state bond lengths in $^1\Sigma - {}^1\Sigma$ bands are generally straightforward. The situation in the present instance is complicated by the fact that the returning R branch carries sufficient intensity to mask the zero gap which establishes the absolute J numbering. We have examined all strong bands and conclude that the ground state of RhP has $B_0'' = 0.204$ cm^{-1}, i.e., $r_0 = 0.186$ nm.

It is instructive to compare the bonding characteristics in RhN and RhF and their 3*p* analogues, RhP and RhCl. Their ground-state molecular parameters are listed in Table 2.

The experimental data indicate that, for RhN and RhP, the dominant ground-state electron configuration is $..\sigma^2\pi^4\delta^4\sigma^2$, where the fully occupied lower σ and π orbitals are bonding, the δ orbital is nonbonding and essentially an atomic Rh 4*d* orbital, and the outer σ orbital is only weakly bonding and predominantly Rh 5*s* in character. In contrast, in the corresponding halides, the ligand-sensitive antibonding π^* orbital is triply occupied ($..\sigma^2\pi^4\delta^4\pi^{*3}\sigma^1$), resulting in the weaker and longer bond.

TABLE 2: Experimental Ground State Molecular Parameters for Some Rhodium Species

molecule	RhN	RhF	RhP	Rh^{35}Cl
symmetry	$^1\Sigma$	$\Omega = 2$	$^1\Sigma$	$\Omega = 2$
vib. spacing/cm^{-1}	897	575	507	∼340
bond length/nm	0.1642	0.1964	0.186	0.2275
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In the electronic transition giving rise to our spectrum, an electron in the highest occupied σ orbital is promoted to a ligand sensitive σ^* antibonding orbital, resulting in an upper state that is less strongly bound. The observed degradation in the rotational structure of the bands indicates an increase in bond length upon electronic excitation of ∼ 0.018 nm.

It is hoped that these results on RhP will provide a stimulus to ab initio theorists to predict the RhP structure as a prelude to calculations on related Rh−P systems of greater complexity.

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