The millimetre-wave spectrum of PH_2Br: first detection of a previously unknown molecule

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The short-lived molecules $PH_2{}^{79}Br$ and $PH_2{}^{81}Br$ are detected for the first time thanks to millimetre-wave spectroscopy allowing determination of accurate rotational and centrifugal distortion constants; these are found to be in good agreement with *ab initio* predictions.

The monohalogenophosphanes PH_2F, PH_2Cl and PH_2I are unstable and short-lived species which have been detected for the first time only recently. It was possible to study all these species by high-resolution IR[1–3] and millimetre-wave spectroscopy.[3,4] At room temperature and a pressure of <2 mbar the halflives of PH_2F, PH_2Cl and PH_2I under collision-controlled conditions were found to be *ca.* 10, 1 and 0.5 min, respectively. Experiments directed towards the detection of the missing species PH_2Br by IR spectroscopy indicate a still shorter lifetime than for the other species.

The present contribution describes the formation and first unambiguous identification of both isotopic species $PH_2{}^{79}Br$ and $PH_2{}^{81}Br$ by millimetre-wave spectroscopy and the determination of the ground-state parameters. The detection was guided by *ab initio* predictions of the rotational parameters[1] whose reliability has been impressively demonstrated for PH_2F, PH_2Cl and PH_2I in the previous studies.[1–4] The potential of millimetre-wave spectroscopy to detect short-lived molecules is indeed well established.[5–8] It combines sensitivity and specificity and provides accurate information on the structure and valuable data related to the molecular force field. The low working pressure is well adapted to unstable species, and enables one to optimize the formation of novel species and to monitor its lifetime.

PH_2Br was synthesized in the gas phase, in analogy with PH_2I, by the reaction of P_2H_4 with HBr at room temp. acording to eqn. (1).

$$P_2H_4 + HBr \rightarrow PH_3 + PH_2Br \qquad (1)$$

The cell was an aluminium oxide tube of 100 cm length and 3 cm inner diameter. It was first filled with P_2H_4 (<0.1 mbar), and then an equivalent amount of HBr was admitted. After the components had been mixed, the measurements were started immediately. Under these conditions the lifetime of PH_2Br allows measurements for about 2 min, then the cell has to be refilled.

The millimetre-wave spectra were measured between 350 and 460 GHz with a computer-controlled source-modulated spectrometer using phase-stabilized submillimetre-wave backward-wave oscillators (Thomson-CSF) as sources and a He-cooled InSb bolometer as detector (QMC). All measurements were made at room temp., and the accuracy of the frequency measurements is generally better than 50 kHz. A small portion of the millimetre-wave spectrum of PH_2Br, together with assignments, is illustrated in Fig. 1.

As the observation interval between two fillings is rather short, it is helpful to have a prediction of the spectrum as accurate as possible. The ground-state rotational constants and the quartic centrifugal distortion constants have been previously calculated *ab initio* at the SCF level[1] using effective core potentials for P and Br. To improve the predictions, we have used the corrections suggested by the previous study of PH_2I,[2] because PH_2Br and PH_2I are similar molecules and *ab initio* calculations were carried out for both molecules using the same basis set at the same level of theory. The estimated correction for the rotational constants B and C of PH_2Br is only 1.5%, the *ab initio* constants being smaller than the experimental ones. For the two centrifugal distortion constants of interest, Δ_J and Δ_{JK}, corrections are 15 and 18%, respectively; here again, the *ab initio* values are smaller than the experimental ones. Since the main component of the dipole moment lies along the a-axis, which is the axis of the least moment of inertia, an a-type rotational spectrum characteristic of a near-symmetric prolate top ($\kappa = -0.99976$) is expected. As $B + C \approx 8.5$ GHz, groups of lines separated by this value are expected for each isotopic species.

In the first trial, we have recorded the spectrum in a frequency range of 7 GHz around 360 GHz and found many lines, most of them being due to by-products and decomposition products. Among the strongest, rapidly decaying lines, it was possible to assign about ten whose fit gave constants in good agreement with the *ab initio* predictions. Then many more lines could be assigned. The good agreement between the experimental and theoretical constants led us to believe that the assigned spectrum belonged to the $PH_2{}^{79}Br$ isotopic species. Thus we first searched for the other isotopic species at lower frequencies. But, as nothing was found, we had to reverse our assignment and we searched at higher frequencies where we could indeed assign the other isotopic species, which is in fact $PH_2{}^{79}Br$. Under the operating conditions (precursors present in the cell, surface effects on the wall), the lifetime is about 2 min, but this may not be the homogeneous lifetime of the pure product which could be much longer.

Because the J values of the measured lines are high ($J > 42$), the nuclear quadrupole hyperfine structure due to the bromine

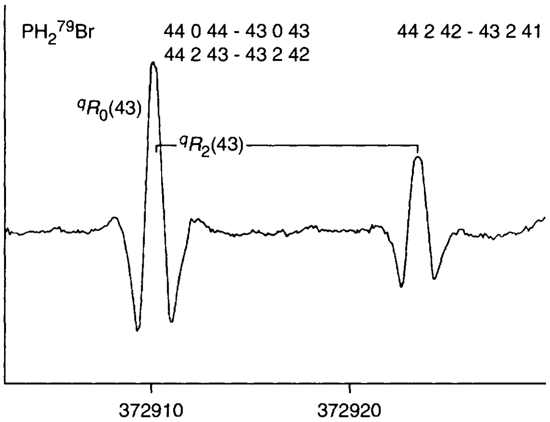

Fig. 1 Example of rotational transitions of $PH_2{}^{79}Br$

Table 1 Ground-state parameters of $PH_2{}^{79}Br$ and $PH_2{}^{81}Br$, *S*-reduction, I^r-representation

	$PH_2{}^{79}Br$			$PH_2{}^{81}Br$
Parameter	*Ab initio*[a]	Experimental	% Diff.[b]	Experimental
A/MHz	132 871.1	129 972(121)	−2.23	129 825(94)
B/MHz	4 161.12	4 252.2 182(15)	2.14	4 221.77 421(93)
C/MHz	4 143.13	4 239.3 750(15)	2.27	4 209.11 400(92)
D_J/kHz	1.798	2.072 531(74)	13.24	2.043154(63)
D_{JK}/kHz	27.915	33.7 670(83)	17.33	33.3 111(85)
D_K/kHz	1 770	1 770[c]		1 770[c]
d_1/Hz	−8.99	−8.07(15)	−11.33	−7.95(10)
d_2/Hz	−0.36	−0.562(35)	35.92	−0.653(29)
H_{JK}/Hz		0.0 313(17)		0.0 271(17)
H_{KJ}/Hz		1.063(48)		1.100(20)
Number of lines		89		60
$J_{min} - J_{max}/K_{max}$		42 − 53/11		42 − 53/13
σ(fit)/kHz		52		23

[a] From ref. 1. [b] 100 (experimental − *ab initio*)/experimental. [c] Fixed at the *ab initio* value.

nucleus was not resolved. As no *c*-type line could be assigned, the *A* rotational constant could not be accurately determined. Both *A*- and *S*-reductions were tried. Although both fits give the same standard deviation and require the same number of fitted parameters, the *S*-reduction gives a much better conditioned system, which is not surprising because PH_2Br is a near-symmetric top. The experimental rotational and centrifugal distortion constants are collected in Table 1 and compared with the *ab initio* predictions. As for PH_2I, there is an excellent consistency between the experimental and *ab initio* rotational constants. The rotational constants of the two isotopic species do not allow us to determine a reliable experimental structure. So, the reported *ab initio* (r_e) structure, r_e(PH) = 1.401 Å, r_e(PBr) = 2.252 Å; α_e(HPH) = 94.6°, γ_e(HPBr) = 97.0°, is presently the best approximation of the equilibrium structure.

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Footnote

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