

Anomalous phosphine sensitivity coefficients as probes for a possible variation of the proton-to-electron mass ratio

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ABSTRACT

A robust variational approach is used to investigate the sensitivity of the rotation–vibration spectrum of phosphine (PH₃) to a possible cosmological variation of the proton-to-electron mass ratio, μ . Whilst the majority of computed sensitivity coefficients, T , involving the low-lying vibrational states acquire the expected values of $T \approx -1$ and $T \approx -1/2$ for rotational and ro-vibrational transitions, respectively, anomalous sensitivities are uncovered for the $A_1 - A_2$ splittings in the ν_2/ν_4 , ν_1/ν_3 and $2\nu_4^{\ell=0}/2\nu_4^{\ell=2}$ manifolds of PH₃. A pronounced Coriolis interaction between these states in conjunction with accidentally degenerate A_1 and A_2 energy levels produces a series of enhanced sensitivity coefficients. Phosphine is expected to occur in a number of different astrophysical environments and has potential for investigating a drifting constant. Furthermore, the displayed behaviour hints at a wider trend in molecules of $C_{3v}(M)$ symmetry, thus demonstrating that the splittings induced by higher-order ro-vibrational interactions are well suited for probing μ in other symmetric top molecules in space, since these low-frequency transitions can be straightforwardly detected by radio telescopes.

Key words: molecular data – cosmological parameters – infrared: ISM – submillimetre: ISM.

1 INTRODUCTION

Recently, the $J = 2 - 1$ rotational transition of phosphine (PH₃) was detected in the carbon star envelope IRC +10216 (Agúndez et al. 2014), thus confirming the presence of PH₃ in the outflows of evolved stars but more significantly outside of the Solar system. The appearance of PH₃ has been predicted in numerous other astrophysical environments (see the discussion by Sousa-Silva et al. 2015 and references therein), and because of prominent ‘irregularities’ displayed by its rotation–vibration spectrum, it is a promising system for investigating the cosmological variability of the proton-to-electron mass ratio, $\mu = m_p/m_e$. Observing PH₃ outside of our Galaxy is no easy feat; however, nearby Galactic molecular clouds offer a means to constrain μ through the so-called chameleon scenario (Brax et al. 2004; Khoury & Weltman 2004) as evidenced by studies of ammonia (Levshakov et al. 2010b,a) and methanol (Daprà et al. 2017).

At present, the most robust constraint on a temporal variation of μ was determined from methanol absorption spectra observed in

the lensing galaxy PKS1830–211 (Kanekar et al. 2015). The three measured transitions possessed sensitivity coefficients, T , ranging from -7.4 to -1.0 and resulted in a constraint of $\dot{\mu}/\mu < 2 \times 10^{-17} \text{ yr}^{-1}$ assuming a linear rate of change. This translates to no change in μ over the past ≈ 7.5 billion years and is in agreement with the best laboratory constraint to date, which measured optical transitions in ¹⁷¹Yb⁺ ions to derive $\dot{\mu}/\mu = (0.2 \pm 1.1) \times 10^{-16} \text{ yr}^{-1}$ (Godun et al. 2014) again assuming a linear rate of change. Whilst the use of methanol has led to several astronomical constraints (Jansen et al. 2011; Levshakov, Kozlov & Reimers 2011; Bagdonaite et al. 2013a,b; Thompson 2013; Kanekar et al. 2015), it is worthwhile identifying other molecular absorbers with notable sensitivities to expand the search for a drifting μ .

Due to the small difference between its rotational constants B and C , and also because of the strong $x - y$ Coriolis interaction between the coinciding ν_2/ν_4 , ν_1/ν_3 and $2\nu_4^{\ell=0}/2\nu_4^{\ell=2}$ states (see Fig. 1), phosphine is a potential candidate system for probing μ . Notably, the spectrum of PH₃, and presumably other molecules of $C_{3v}(M)$ symmetry, is special due to the anomalous behaviour of the $A_1 - A_2$ splittings (Ulenikov et al. 2002). A large number of spectroscopic studies of PH₃ have been reported in the literature (see Müller 2013 and references therein) and highly accurate data is available for the majority of its states. Furthermore,

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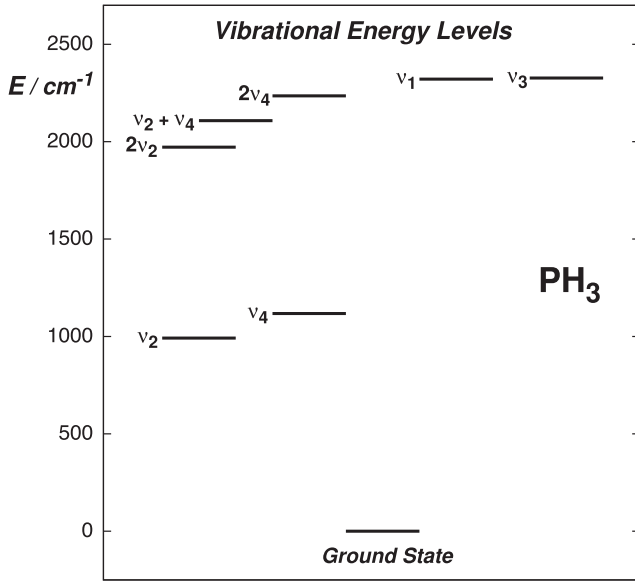


Figure 1. The lowest vibrational energy levels of PH₃.

a robust theoretical description of this molecule, which we utilize for this work, has been developed over the years (Yurchenko et al. 2003, 2005, 2006; Ovsyannikov et al. 2008a,b; Sousa-Silva, Yurchenko & Tennyson 2013; Sousa-Silva et al. 2014, 2015; Sousa-Silva, Tennyson & Yurchenko 2016), culminating in the construction of a comprehensive rotation–vibration line list applicable for elevated temperatures (Sousa-Silva et al. 2015).

Model radiative transfer calculations of phosphine excitation in the envelope of IRC +10216 (Cernicharo et al. 1999; Agúndez et al. 2014) highlighted the importance of infrared pumping from the ground to the first excited vibrational states, helping explain the presence of strong emission bands in the observed spectra. We therefore find it useful to investigate the sensitivity of the ground, fundamental and low-lying combination and overtone vibrational states of PH₃ (see Fig. 1) to a possible space–time variation of μ using a robust variational approach. The paper is structured as follows: in Section 2, we describe the variational approach used to compute sensitivity coefficients. The results for the phosphine molecule are presented and discussed in Section 3. Concluding remarks are given in Section 4.

2 VARIATIONAL APPROACH

The sensitivity coefficient $T_{u,l}$ between an upper and lower state with energy E_u and E_l , respectively, is defined as

$$T_{u,l} = \frac{\mu}{E_u - E_l} \left(\frac{dE_u}{d\mu} - \frac{dE_l}{d\mu} \right), \quad (1)$$

and can be related to the induced frequency shift of a transition, or energy difference $E_u - E_l$ between two states, through the expression

$$\frac{\Delta\nu}{\nu_0} = T_{u,l} \frac{\Delta\mu}{\mu_0}, \quad (2)$$

where $\Delta\nu = \nu_{\text{obs}} - \nu_0$ is the change in the frequency, and $\Delta\mu = \mu_{\text{obs}} - \mu_0$ is the change in μ , both with respect to their present-day values ν_0 and μ_0 . By assuming all baryonic matter can be treated equally (Dent 2007), μ is proportional to the molecular mass. One can then perform a series of calculations with suitably

scaled values for the masses of the P and H atoms and extract numerical values for the derivatives $dE/d\mu$ using central finite differences.

Sensitivity coefficients for PH₃ have been computed with the same variational approach as was previously employed for ammonia (Owens et al. 2015a, 2016) and the hydronium cation (Owens et al. 2015b). Calculations were carried out with the nuclear motion program TROVE (Yurchenko, Thiel & Jensen 2007; Yachmenev & Yurchenko 2015; Yurchenko, Yachmenev & Ovsyannikov 2017) and utilized the potential energy surface (PES), dipole moment surface (DMS) and computational set-up of Sousa-Silva et al. (2015), which have all undergone rigorous testing and are known to be reliable. We refer the reader to Sousa-Silva et al. (2015) for further details of the nuclear motion computations. All sensitivity coefficients, equation (1), have been determined with calculated frequencies, $E_u - E_l$, as oppose to experimental values when available. This was done for consistency and to verify the trend in sensitivities displayed by PH₃, which we will discuss further in Section 3.

3 RESULTS AND DISCUSSION

In general, as shown in Table 1, Figs 2 and 3, the majority of the calculated sensitivity coefficients for the low-lying vibrational states acquire the expected values of $T \approx -1$ and $T \approx -1/2$ for rotational and ro-vibrational transitions, respectively. Notably, this is the case for the $J = 2 - 1$ and $J = 1 - 0$ rotational transitions observed in the carbon star envelope IRC +10216 (Agúndez et al. 2008, 2014). For a small fraction of the probed transitions, the sensitivities deviate from the usual values. Accidental coincidences between ro-vibrational states can cause the magnitude of these ‘irregularities’ to strongly increase with vibrational excitation, as illustrated in Fig. 4.

The most striking sensitivities are displayed by the $A_1 - A_2$ doublets of PH₃. As is well known for a molecule with $C_{3v}(M)$ symmetry, all rotation–vibration energy levels corresponding to the same $K \equiv |k| \neq 0$ rotational quantum number and having overall A_1, A_2 symmetry are split into doublets due to different ro-vibrational interactions (see, for example, Chen & Oka 1989). For the non-degenerate vibrational states, the $A_1 - A_2$ splittings occur for rotational levels with $K = 3n$ ($n = 1, 2, \dots$). For the doubly degenerate fundamental vibrational states characterized by the vibrational angular momentum quantum number $\ell \neq 0$, the splittings occur for the $K = 1, 2, 4, 5, 7, 8, \dots$ levels.

In Tables 2–9, we have computed sensitivity coefficients for a large number of the $A_1 - A_2$ doublets for low-lying vibrational states. The results suggest that sensitivities of the $A_1 - A_2$ splittings for non-coinciding ro-vibrational states possess values dependent on the rotational quantum number J . For example, $T \approx -1.5, -2, -3$ for $k = 1, 2, 3$, respectively (see Tables 2–5). It would be interesting to see if this trend is present in other molecules of $C_{3v}(M)$ symmetry. For the sensitivities corresponding to coinciding states, there is a strong and irregular dependence on the $x - y$ Coriolis interaction that can produce values at least one order of magnitude larger than the respective Coriolis-free predictions. This behaviour is similar to that of NH₃ (Špirko 2014; Owens et al. 2015a, 2016) and H₃O⁺ (Owens et al. 2015b).

A detailed study of the $A_1 - A_2$ splittings in the $2\nu_4^{\ell=2}$ state was presented by Ulenikov et al. (2002) where it was shown that the dependence of the splitting on J in the $K = 1$ rotational sub-levels was anomalous between $J = 3-8$. This anomaly is caused by an interaction with the closely lying $2\nu_4^{\ell=0}$ state ($K = 0$). In Fig. 5 and Table 9, we show the $A_1 - A_2$ splittings in the $2\nu_4^{\ell=2}$ state and corresponding sensitivity coefficients with respect to J . Aside from the $J = 7$ sensitivity coefficient, which greatly increases when

Table 1. Calculated frequency ν_{calc} (in MHz), frequency difference Δ_{c-e} (in MHz) compared to experimental value from Belov et al. (1981), Einstein A coefficient (in s^{-1}) and sensitivity coefficient T for vibrational ground-state transitions of PH_3 .

Γ'	J'	K'	Γ''	J''	K''	ν_{calc}	Δ_{c-e}	A	T
Allowed									
A_2	1	0	A_1	0	0	266 947.2	2.7	0.253E-04	-0.99
E	2	1	E	1	1	533 819.4	4.2	0.182E-03	-0.99
A_1	2	0	A_2	1	0	533 795.5	0.9	0.242E-03	-1.00
E	3	2	E	2	2	800 586.8	6.9	0.486E-03	-1.00
E	3	1	E	2	1	800 490.8	3.7	0.778E-03	-0.99
A_2	3	0	A_1	2	0	800 463.8	7.7	0.875E-03	-0.99
A_1	4	3	A_2	3	3	1067 210.2	3.9	0.940E-03	-0.99
A_2	4	3	A_1	3	3	1067 210.2	3.9	0.940E-03	-0.99
E	4	2	E	3	2	1067 006.3	6.0	0.161E-02	-0.99
E	4	1	E	3	1	1066 886.4	9.5	0.201E-02	-1.00
A_1	4	0	A_2	3	0	1066 844.4	8.5	0.215E-02	-1.00
Forbidden									
E	6	1	E	6	2	47 409.2	18.0	0.780E-12	-0.87
E	7	1	E	7	2	47 199.3	20.7	0.140E-11	-0.95
E	8	1	E	8	2	46 962.5	23.4	0.232E-11	-0.96
E	9	1	E	9	2	46 695.7	24.2	0.362E-11	-1.08
E	10	1	E	10	2	46 404.9	27.1	0.540E-11	-0.85
E	11	1	E	11	2	46 090.1	31.6	0.775E-11	-0.85
E	12	1	E	12	2	45 748.3	33.5	0.108E-10	-0.86
E	13	1	E	13	2	45 382.6	34.7	0.146E-10	-0.83
E	14	1	E	14	2	44 995.8	37.2	0.193E-10	-0.96
E	15	1	E	15	2	44 591.1	42.2	0.251E-10	-0.92
A_2	3	0	A_1	3	3	143 750.5	48.9	0.152E-11	-0.98
A_1	4	0	A_2	4	3	143 384.7	53.7	0.636E-11	-1.01
A_2	5	0	A_1	5	3	142 923.1	53.1	0.169E-10	-1.01
A_1	6	0	A_2	6	3	142 377.4	58.4	0.361E-10	-0.96
A_2	7	0	A_1	7	3	141 744.9	65.8	0.674E-10	-0.96
A_1	8	0	A_2	8	3	141 022.4	71.9	0.115E-09	-0.96
A_2	9	0	A_1	9	3	140 209.9	76.8	0.182E-09	-0.96
A_1	10	0	A_2	10	3	139 307.6	81.0	0.275E-09	-0.97
A_2	11	0	A_1	11	3	138 318.2	90.2	0.398E-09	-0.95
A_1	12	0	A_2	12	3	137 230.0	95.3	0.557E-09	-0.93
A_2	13	0	A_1	13	3	136 045.8	104.4	0.756E-09	-0.90
A_1	14	0	A_2	14	3	134 750.7	109.3	0.100E-08	-0.93
E	6	2	E	6	5	333 977.8	137.8	0.903E-10	-0.99
E	7	2	E	7	5	332 493.8	148.9	0.225E-09	-0.97
E	8	2	E	8	5	330 815.0	163.3	0.452E-09	-0.97
E	9	2	E	9	5	328 941.3	176.9	0.801E-09	-0.96
E	10	2	E	10	5	326 884.7	194.4	0.130E-08	-0.98
E	11	2	E	11	5	324 645.2	209.3	0.199E-08	-0.95
E	12	2	E	12	5	322 237.9	228.9	0.290E-08	-0.95
E	13	2	E	13	5	319 665.7	247.9	0.406E-08	-0.96
E	14	2	E	14	5	316 940.6	268.7	0.552E-08	-0.93
E	15	2	E	15	5	314 068.6	288.1	0.731E-08	-0.92
A_1	7	3	A_2	7	6	429 296.8	188.4	0.249E-09	-0.99
A_2	7	3	A_1	7	6	429 284.8	189.2	0.249E-09	-1.00
A_1	8	3	A_2	8	6	427 132.3	205.7	0.613E-09	-0.98
A_2	8	3	A_1	8	6	427 105.3	207.2	0.613E-09	-0.98
A_1	9	3	A_2	9	6	424 728.0	227.1	0.122E-08	-0.98
A_2	9	3	A_1	9	6	424 671.0	227.0	0.122E-08	-0.98
A_1	10	3	A_2	10	6	422 092.8	249.8	0.213E-08	-0.96
A_2	10	3	A_1	10	6	421 984.9	247.2	0.213E-08	-0.96
A_1	11	3	A_2	11	6	419 238.8	271.7	0.343E-08	-0.96
A_2	11	3	A_1	11	6	419 052.9	269.8	0.343E-08	-0.96
A_1	12	3	A_2	12	6	416 186.9	297.6	0.519E-08	-0.95
A_2	12	3	A_1	12	6	415 878.1	294.8	0.518E-08	-0.94
A_1	13	3	A_2	13	6	412 949.1	320.2	0.748E-08	-0.94
A_2	13	3	A_1	13	6	412 457.5	316.6	0.747E-08	-0.95
A_1	14	3	A_2	14	6	409 558.5	350.2	0.104E-07	-0.94
A_2	14	3	A_1	14	6	408 797.0	341.3	0.104E-07	-0.94
A_1	15	3	A_2	15	6	406 029.9	377.3	0.140E-07	-0.93
A_2	15	3	A_1	15	6	404 893.7	366.7	0.139E-07	-0.92

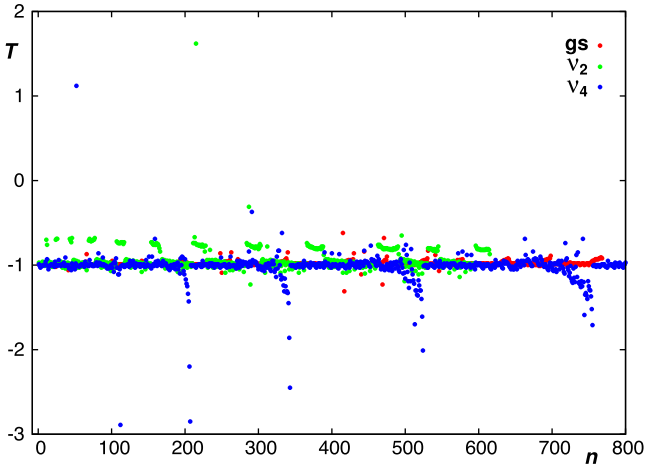


Figure 2. Sensitivity coefficients T for pure rotational transitions in the ground, ν_2 , and ν_4 vibrational states of PH₃. Here, n is a running number which counts the number of transitions.

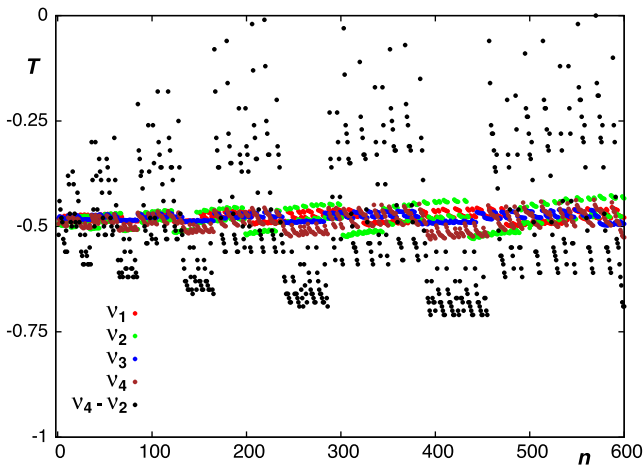


Figure 3. Sensitivity coefficients T for ro-vibrational transitions from the ground to the lowest vibrational states of PH₃. Here, n is a running number which counts the number of transitions.

using the experimental frequency value, there is good agreement with the work of Ulenikov et al. (2002) and the sensitivities are highly anomalous.

It should be stated that for very energetically close coinciding states, our variational approach may not be capable of a truly quantitative description. This is the reason why sensitivities have not been computed for certain extremely small $A_1 - A_2$ splittings. Also, where computed frequencies noticeably differ from the experimental values the resultant sensitivities should only be regarded as illustrative, for example, in Table 8. We have encountered this problem before (Owens et al. 2016) and whilst the underlying numerical derivatives are relatively stable, it is safer to regard the predicted sensitivity coefficients with caution. Despite this, a large number of the computed $A_1 - A_2$ splittings are in good agreement with experiment and, more importantly, reside in the radio frequency region.

4 CONCLUSION

The sensitivity of the rotation–vibration spectrum of PH₃ to a possible variation of μ has been probed using an accurate variational

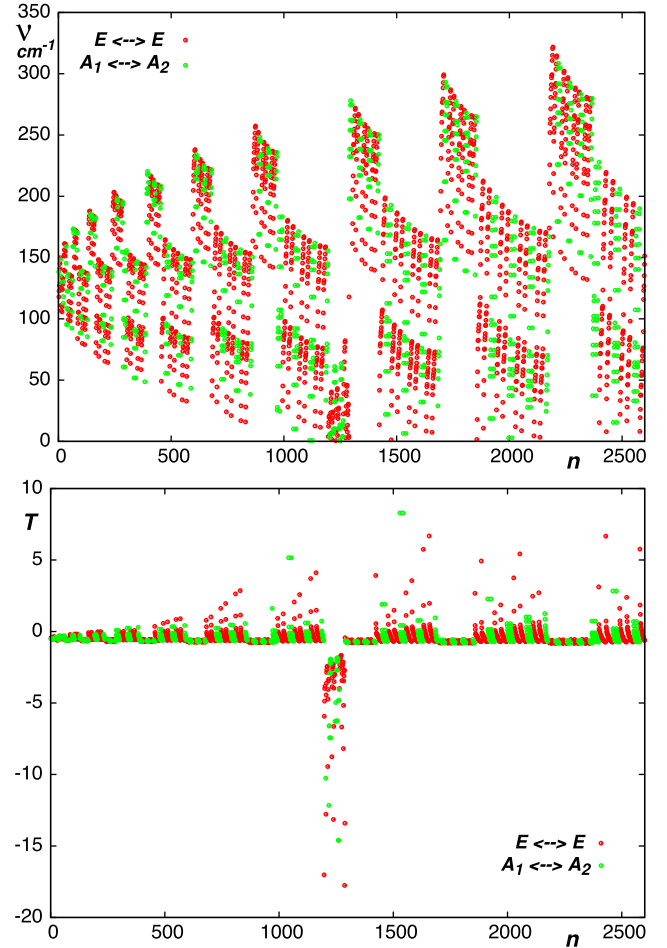


Figure 4. The wavenumbers ν (in cm^{-1}) and sensitivity coefficients T of the $\nu_4 \leftarrow \nu_2$ ro-vibrational transitions of PH₃. Here, n is a running number which counts the number of transitions.

Table 2. Calculated and experimental $k = 3$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ground (gs) and ν_2 vibrational states of PH₃.

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	gs			ν_2		
4	0.43409 ^a	0.450		3.60 ^b	3.568	
5	1.73413 ^a	1.769		13.096 ^b	13.371	
6	5.19570 ^a	5.246		36.627 ^b	37.384	
7	12.9690 ^a	13.101		78 ^c	86.640	− 3.6
8	28.4825 ^a	28.780	− 2.9	174 ^c	176.19	− 3.6
9	56.8550 ^a	57.440	− 2.7	318 ^c	325.12	− 3.5
10		106.46	− 2.90	531 ^c	557.13	− 3.4
11		185.90	− 3.00	872 ^c	900.40	− 3.3
12		309.03	− 3.02	1412 ^c	1388.2	− 3.3
13		493.04	− 3.04	2009 ^c	2059.6	− 3.3
14		759.76	− 3.03	2896 ^c	2959.6	− 3.17
15		1136.1	− 3.02	4686 ^c	4139.8	− 3.13
16		1654.8	− 3.03		5660.3	− 3.10
17		2355.8	− 3.03		7588.6	− 3.07
18		3285.9	− 3.03		10002	− 3.06

^aDavies et al. (1971), ^bChen & Oka (1989), ^cPapoušek et al. (1989).

Table 3. Calculated and experimental (Ulenikov et al. 2002) $k = 3$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ν_1 and $2\nu_4^{\ell=2}$ vibrational states of PH_3 .

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	ν_1			$2\nu_4^{\ell=2}$		
4		2.10		573	503.6	-2.6
5		7.88		1811	1561	-2.6
6		21.62		3906	3337	-2.5
7		47.37	-5	6763	5792	-2.33
8	45	87.18	-3.8	9719	8885	-2.25
9	114	140.0	-3.84	14 429	12 504	-2.15
10		201.9	-2.97	17 649	15 241	-1.54
11	195	261.9	-2.05	19 460	17 519	-3.17
12	342	480.0	-3.38	29 539	26 118	-2.15
13	255	810.2	-3.65		32 465	-2.03
14	6706	959.2	21.3		38 781	-1.98
15		6665	3.83		45 247	-1.89
16		1756	-14.17		51 606	-1.86
17		3405	-5.39		57 544	-1.76
18		5880	-10.61		52 187	0.15

Table 4. Calculated and experimental $k = 1$ and $k = 2$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ν_4 vibrational state of PH_3 .

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	$k = 1$			$k = 2$		
1	10 498.9 ^a	10 429.5	-1.51			
2	31 269.7 ^a	31 058.4	-1.50	30 ^b	30.16	
3	61 876.0 ^c	61 444.7	-1.49	150 ^b	149.12	-2.51
4	101 889.7 ^d	101 152	-1.48	438 ^b	436.62	-2.37
5	150 200 ^e	149 480	-1.47	986 ^b	975.97	-2.35
6	207 700 ^e	205 747	-1.45	1850 ^b	1827.4	-2.37
7	271 300 ^e	269 219	-1.44	3034 ^b	3004.9	-2.32
8	342 600 ^e	339 148	-1.43	4521 ^b	4471.7	-2.22
9	419 000 ^e	414 689	-1.40	6175 ^b	6156.9	-2.17
10	502 300 ^e	497 112	-1.38	7989 ^b	7980.1	-2.11
11	588 700 ^e	581 763	-1.37	9875 ^b	9868.3	-2.03
12	679 300 ^e	671 136	-1.35	11 700 ^e	11 762	-1.97
13	772 300 ^e	764 108	-1.34	12 600 ^e	13 613	-1.93
14	869 600 ^e	860 215	-1.32	17 900 ^e	15 378	-1.88
15	967 700 ^e	959 068	-1.31	19 600 ^e	16 754	-1.68
16		1060 200	-1.30		12 454	-4.48
17		1162 100	-1.27		18 172	-1.81
18		1273 400	-1.27		19 568	-1.67

^aScappini & Schwarz (1981), ^bPapoušek et al. (1989), ^cGuarnieri, Scappini & Di Lonardo (1981), ^dBelov et al. (1983), ^eTarrago, Dang-Nhu & Goldman (1981).

approach. Calculations utilized the nuclear motion program TROVE in conjunction with an established empirically refined PES and *ab initio* DMS. The low-lying vibrational states were studied as they play an important role in phosphine excitation in the carbon star envelope IRC +10216. Whilst the majority of computed sensitivity coefficients assumed their expected values, anomalous sensitivities were displayed by the $A_1 - A_2$ splittings in the ν_2/ν_4 , ν_1/ν_3 and $2\nu_4^{\ell=0}/2\nu_4^{\ell=2}$ manifolds. This behaviour arises due to strong Coriolis interactions between states and may be present in other molecules with $C_{3v}(M)$ symmetry. The fact that molecules with highly sensitive transitions such as ammonia are already being used in advanced terrestrial experiments (Cheng et al. 2016) suggests that PH_3 may not be a primary candidate for constraining μ in laboratory studies.

Table 5. Calculated and experimental (Ulenikov et al. 2002) $k = 1$ and $k = 2$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ν_3 vibrational state of PH_3 .

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	$k = 1$			$k = 2$		
1	333	533	-1.57			
2	1004	1596	-1.45	54	59.48	-3.7
3	2015	3177	-1.46	288	293.89	-3.4
4	3385	5256	-1.45	914	864.93	-3.22
5	5081	7788	-1.46	2078	1959.3	-3.13
6	7069	10 686	-1.44	3990	3747.7	-3.08
7	9156	13 763	-1.38	6799	6301.6	-2.96
8	11 368	16 604	-1.20	10 460	9453.3	-2.75
9	12 825	18 371	-0.79	14 558	12 583	-2.36
10	12 894	37 630	-0.72	18 386	34 468	-1.61
11	10 736	41 212	-0.86	21 441	42 221	-1.95
12	39 033	45 466	-0.84	56 796	52 692	-2.17
13	44 078	49 330	-0.61	71 518	66 005	-2.41
14	49 924	51 045	0.08		83 884	-2.99
15	51 214	48 059	0.58		224 180	1.45
16		34 359	-32.8		73 345	-7.15
17		128 720	3.81		86 681	5.34
18		128 190	-1.23		110 930	-3.44

Table 6. Calculated and experimental (Ulenikov et al. 2002) $k = 4$ and $k = 5$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ν_3 vibrational state of PH_3 .

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	$k = 4$			$k = 5$		
8		97.79	-2.94			
9		295.8	-2.70			
10	563	889.3	-2.81		135.1	-2.87
11	2215	2988	-2.36	186	267.1	-2.81
12	5546	35905	-2.45	216	278.9	2.02
13	3439	6242	-2.91	306	16.1	461
14	3663	6172	-5.8		6171	-25.50
15		6098	-5.4		15175	18.1

Table 7. Calculated and experimental $k = 4$ and $k = 7$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ν_4 vibrational state of PH_3 .

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	$k = 4$			$k = 7$		
5	582 ^a	582.08	-2.08			
6	1292 ^a	1310.2	-2.18			
7	2278 ^a	2418.6	-2.13			
8	3897 ^a	3916.4	-2.15			
9	5762 ^a	5788.4	-2.11	210 ^b	211.7	-5.25
10	7971 ^a	8019.5	-2.08	1190 ^b	1363.3	1.04
11	10 530 ^a	10 610	-2.07	618 ^b	646.3	-2.09
12	13 730 ^a	13 580	-2.06	651 ^b	671.4	-2.33
13	16 793 ^a	16 966	-2.06	767 ^b	796.7	-2.54
14	20 686 ^a	20 821	-2.08	959 ^b	987.3	-2.67
15	23 800 ^c	25 211	-2.09	1157 ^b	1246.5	-2.71
16		30 209	-2.10		1589.1	-2.84
17		35 900	-2.12		2038.3	-2.87
18		42 378	-2.15		2625.3	-2.94

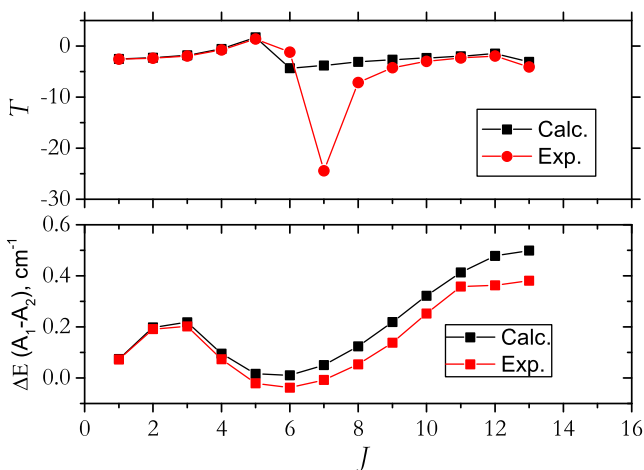
^aDavies et al. (1971), ^bPapoušek et al. (1989), ^cChen & Oka (1989).

Table 8. Calculated and experimental (Ulenikov et al. 2002) $k=7$ and $k=8$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the ν_3 vibrational state of PH₃.

J	ν_{exp}	ν_{calc}	T	ν_{exp}	ν_{calc}	T
	$k=7$			$k=8$		
12		30.55	-64	1340	743.7	-91
13		1260170	1.44		18210	34
14	1817	8766	0.21	3136	10565	-4.91
15		2585.5	27.6		1344.4	-22.3
16		807.4	-1.11		1370.2	11.7
17		1485.1	-22.9		5056.4	-16.8
18		1315.0	-417		73.0	-3.1

Table 9. Calculated and experimental (Ulenikov et al. 2002) $k=1$, $A_1 - A_2$ splittings (in MHz) and their sensitivities in the $2\nu_4^{\ell=2}$ vibrational state of PH₃. The splitting $\nu = \Delta E_{A_1/A_2} = (E_{A_2} - E_{A_1}) \cdot (-1)^J$. The sensitivity T_{exp} is obtained using the frequencies from Ulenikov et al. (2002) instead of the computed values.

J	ν_{calc}	T_{calc}	ν_{exp}	T_{exp}
1	221.7055	-2.5	216.7499	-2.6
2	592.9445	-2.3	573.2032	-2.4
3	653.0709	-1.8	604.0818	-1.9
4	286.2628	-0.6	220.3475	-0.7
5	48.8692	1.7	-62.0570	1.4
6	31.0615	-4.3	-115.4201	-1.2
7	150.8825	-3.8	-23.3838	-24.4
8	370.1448	-3.1	160.3890	-7.2
9	656.5515	-2.7	413.1140	-4.2
10	964.8880	-2.3	757.2757	-3.0
11	1240.5502	-2.0	1072.9572	-2.3
12	1432.5733	-1.5	1087.6470	-1.9
13	1495.6166	-3.1	1141.3099	-4.1

**Figure 5.** The $A_1 - A_2$ splittings in the $2\nu_4^{\ell=2}$ state of PH₃ (lower panel) and the corresponding sensitivities T (upper panel). The experimentally determined energies by Ulenikov et al. (2002) were used in equation (1) to estimate the T_{exp} values.

Its merit as a probe for a drifting constant is more likely to be in cosmological settings as it is a relevant astrophysical molecule with a well-documented spectrum and a negligible hyperfine splitting (Müller 2013). However, it is hard to comment on the necessary conditions for its detection since its presence and formation are

not well understood (see the discussion by Sousa-Silva et al. 2015 and references therein). Despite this, PH₃ as a model system shows that the splittings caused by higher-order rotation–vibration interactions, which are essentially low-frequency transitions that can be measured using radio telescopes, have real potential for investigating a possible variation of μ .

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