THE ASTROPHYSICAL JOURNAL, 464:L203–L206, 1996 June 20

LASER MAGNETIC RESONANCE MEASUREMENT OF THE $^3P_1$–$^3P_0$ FINE-STRUCTURE SEPARATION OF P^+

JOHN M. BROWN
Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, England
K. M. EVENSON AND LYNDON R. ZINK
Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway Street, Boulder, CO 80303
AND
ELZA C. C. VASCONCELLOS
Instituto de Física "Gleb Wataghin," Departamento de Electrônica Quântica, Universidade Estadual de Campinas, 13083-970 Campinas, SP, Brazil
Received 1996 February 12; accepted 1996 April 4

ABSTRACT

The far-infrared laser magnetic resonance spectrum associated with the $J = 1 \leftarrow 0$ fine-structure transition of $^{31}P^+$ in its ground ^3P state has been recorded. This is the first laboratory observation of this magnetic dipole transition, and its frequency has been measured 2 orders of magnitude more accurately than the previous, indirect determination from optical spectroscopy. The frequency is $\Delta E_{10} = 4944433.0 \pm 1.7$ MHz. A small nuclear hyperfine splitting was also observed for the $J = 1$ level.

Subject heading: atomic data

1. INTRODUCTION

The atomic P^+ ion (P II) has a regular fine structure in its ground ^3P state, which arises from the $3s^2 3p^2$ electronic configuration (isoelectronic with atomic silicon). In this Letter, we report a direct laboratory observation of the $J = 1 \leftarrow 0$ fine-structure transition, which is magnetic dipolar in character. The observation was made by laser magnetic resonance (LMR) in the far-infrared and yields an accurate transition frequency of 4944433.0 ± 1.7 MHz.

Atomic fine-structure transitions are useful probes of the local physical conditions in various astrophysical situations. For example, the fine-structure transitions in C^+ (^2P) at 158 μm and in N^+ (^3P) at 122 and 205 μm are prominent in emission from the gaseous component of the interstellar medium (Wright et al. 1991); the signals provide information on the large-scale structure of our Galaxy. Similarly, the fine-structure transition in S (^3P) at 25.2 μm provides an important diagnostic for interstellar shocks (Tielens & Hollenbach 1985; Haas, Holenbach, & Erickson 1991). The fine-structure intervals of light atoms fall in the far-infrared region of the electromagnetic spectrum. Many of them have been determined within an uncertainty of ~1 GHz from differences between lines in optical spectra (Moore 1949). In recent years, such transitions have been detected directly in astrophysical sources by either heterodyne or Fabry-Perot interferometric techniques. The observations point to a need for more accurate determinations of the rest frequencies of the transitions. If the observation is to be used to measure, e.g., the relative velocities of different components of interstellar gas, the rest frequency needs to be known within a few megahertz, as shown by the measurements on C^+ by Lugten et al. (1986).

A program to measure these intervals by far-infrared LMR spectroscopy has been established at the Boulder laboratories of the National Institute of Standards and Technology. A new microwave discharge source to generate the atoms has been developed (Varberg, Brown, & Evenson 1994), and the operation of the far-infrared laser has been extended to shorter wavelengths. As a result, we have recently been able to report the accurate measurement of the fine-structure intervals for several atoms, many of which are important in astrophysics. These include O (Brown, Evenson, & Zink 1993), S (Brown, Evenson, & Zink 1994a), and N^+ (Brown et al. 1994b). Our measurement of the $^3P_1$–$^3P_0$ fine-structure interval of P^+ will facilitate astronomical searches for this species. Since phosphorus has an extremely low cosmic abundance ($<10^{-10}$ relative to H), its detection might be thought unlikely. However, the diatomic molecules PN and CP have both been detected in the interstellar medium (Turner & Bally 1987; Ziurys 1987; Guélin et al. 1990). There is a distinct possibility that the element appears to be depleted because it exists mostly in the form of nonvolatile compounds. Atomic phosphorous has a comparatively low ionization potential (10.49 eV) and so may be formed easily in ionized regions.

2. EXPERIMENTAL DETAILS AND RESULTS

The details of the LMR apparatus have been given in our earlier papers (e.g., Brown et al. 1994a). As described there, the performance has been enhanced in two ways: (1) by increased sensitivity and (2) by operation at shorter wavelengths. The P^+ ions were generated in the gas phase using the same microwave discharge source as we used to form N^+ ions (see Brown et al. 1994b). The discharge was run through ultra–high-purity helium at 93 Pa (0.7 torr) with a small amount of phosphorous trifluoride, PF_3, added; the optimum pressure of PF_3 was 0.7 Pa (5 mtorr).

The energy level diagram of P^+ in its ground ^3P state is shown in Figure 1. The $J = 1 \leftarrow 0$ transition has been detected with a newly discovered laser line in CH_3OH at 60.68 μm (Vasconcellos et al. 1995), which falls close to the best available estimate of the fine-structure interval from optical spectroscopy of 164.90 cm^{-1} (4943.6 GHz, or 60.64 μm) by Martin, Zalubas, & Musgrove (1995; see also Svendenius, Magnusson, & Zetterberg 1983). The CH_3OH laser line is pumped by the $10R(52)$ line of the carbon dioxide laser; its frequency has recently been measured to be 4490907.5 ± 1.0 MHz.

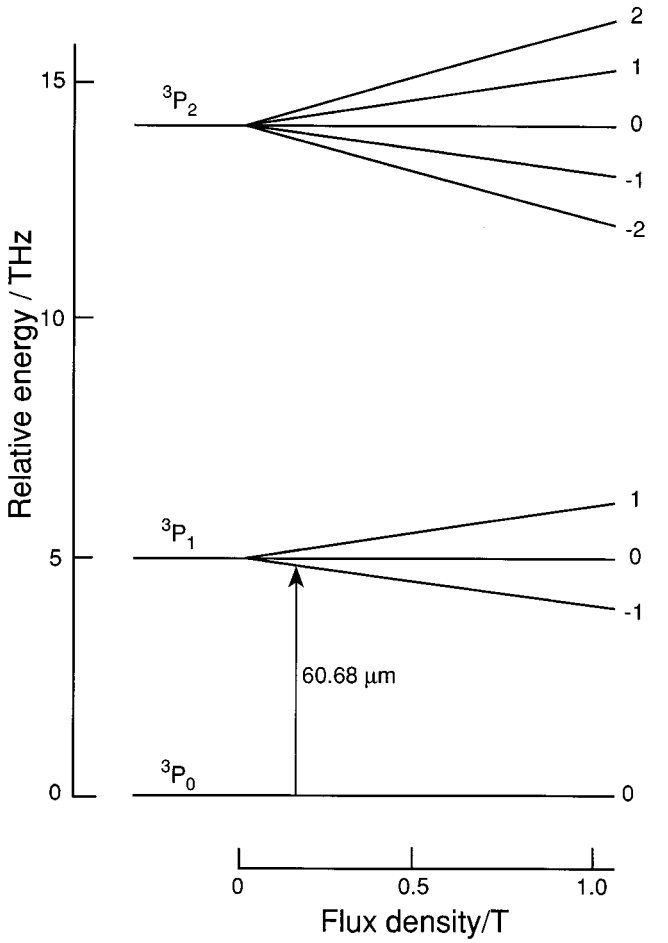

FIG. 1.—Energy level diagram for the P^+ ion in its ground ^3P state, in the presence of a variable magnetic field. The Zeeman components are labeled by their M_J-values. The Zeeman splittings are exaggerated for the sake of clarity. The observed transition between the $J = 1$ and 0 components is shown.

As can be seen from Figure 1, the LMR spectrum associated with the $J = 1 \leftarrow 0$ fine-structure transition of an atom in a ^3P state consists of a single transition, $M_J = -1 \leftarrow 0$ (or $1 \leftarrow 0$ if the laser frequency is higher than the atomic interval). The observed spectrum, shown in Figure 2, is in fact a closely spaced doublet. This doubling can be attributed to nuclear hyperfine structure involving the ^{31}P nucleus ($I = \frac{1}{2}$); the splitting is expected to be approximately zero in first order, as discussed below. The magnitude of the resonant magnetic field and the observation of hyperfine splitting leave little doubt that the spectrum arises from P^+. Additional confirmation was provided by laser frequency pulling experiments, which showed that the signals tune negatively (i.e., as the frequency increases, the resonance shifts to lower flux densities). The resonant flux densities were measured, and the results are listed in Table 1.

A complete description of the M_J-levels of an atom in a ^3P state requires several parameters (see, e.g., Cooksy, Hovde, & Saykally 1986). The observed resonances associated with the $J = 1 \leftarrow 0$ transition depend primarily on three parameters, ΔE_{10}, $g_{J=1}$, and A_1, the last of which is is the diagonal magnetic hyperfine parameter for the $J = 1$ level. Since we have only two pieces of data, we have chosen to estimate the value of the

TABLE 1

FAR-INFRARED LASER MAGNETIC RESONANCE DATA FOR $^{31}P^+$ ATOMS

J	M_J	M_I[a]	ν_L[b] (GHz)	B_0[c] (mT)
$1 \leftarrow 0\ldots$	$-1 \leftarrow 0$	$-\frac{1}{2}$	4940.9075	167.16
	$-1 \leftarrow 0$	$\frac{1}{2}$	4940.9075	168.54

[a] The transitions obey the selection rule $\Delta M_I = 0$.
[b] The 60.68 μm line of CH_3OH, pumped by the $10R(52)$ line of a CO_2 laser. This frequency, as used in the experiment, has an uncertainty of 1.5 MHz.
[c] Measurement uncertainties = 0.05 mT.

g-factor $g_{J=1}$ and hence determine values for the other two parameters. The g-factors can be estimated quite reliably under the assumption of a Russell-Saunders coupling scheme. In practice, we have used the values measured for the isoelectronic silicon atom (Brown, Zink, & Evenson 1994c). The values determined for ΔE_{10} and A_1 in this way are listed in Table 2. As a final check, a full calculation for P^+ in the ^3P state was performed using the values for the remaining, insignificant parameters taken from other work; the details are also given in Table 2. The hyperfine parameters are derived from those of ^{29}Si (Brown et al. 1994c), suitably scaled in the ratio of the A_1-values. Note that the sign of the corresponding parameters for the two atoms are opposite; this reflects the difference in sign of the magnetic moments of the two nuclei. The M_I assignments given to the transitions in Table 1 are based on this predicted sign of the parameter A_1. There are three contributions to A_1, two large ones from the magnetic fields at the nucleus created by the orbital and spin motion of the open shell electrons, which, to a close approximation, cancel each other out, and a very small one from the electron spin density at the nucleus, the contact interaction (Cooksy et al. 1986). The balance between these contributions may be altered in P^+, and as a result, A_1 may have the opposite sign from that assumed in Table 2.

Because of the paucity of data on P^+ from its LMR spectrum, the uncertainty in the parameters determined must be estimated. For the fine-structure interval, which is obtained by extrapolation to zero magnetic field, there are three inde-

TABLE 2

PARAMETERS USED TO DESCRIBE THE FAR-INFRARED LASER MAGNETIC RESONANCE SPECTRUM OF $^{31}P^+$

Parameter	Value	Reference
ΔE_{10} (GHz)	4944.4330 (17)[a]	1
ΔE_{21} (GHz)	9120.3	2
$g_{J=1}$	1.50079[b]	3
$g_{J=2}$	1.50064[b]	3
A_1 (MHz).....	−28.56 (42)[a, c]	1
A_2 (MHz).....	2497[d]	3
A_{10} (MHz).....	1375[d]	3
A_{21} (MHz).....	1579[d]	3

[a] Uncertainty (1 σ) estimated from experimental and model errors (see § 2), in units of the last quoted decimal place.
[b] Value for ^{28}Si atom.
[c] The sign of the parameter A_1 has been assumed; see § 2.
[d] Value scaled from that for ^{29}Si, in the ratio of the A_1-values.

REFERENCES.—(1) This Letter; (2) Martin et al. 1985; (3) Brown et al. 1994a.

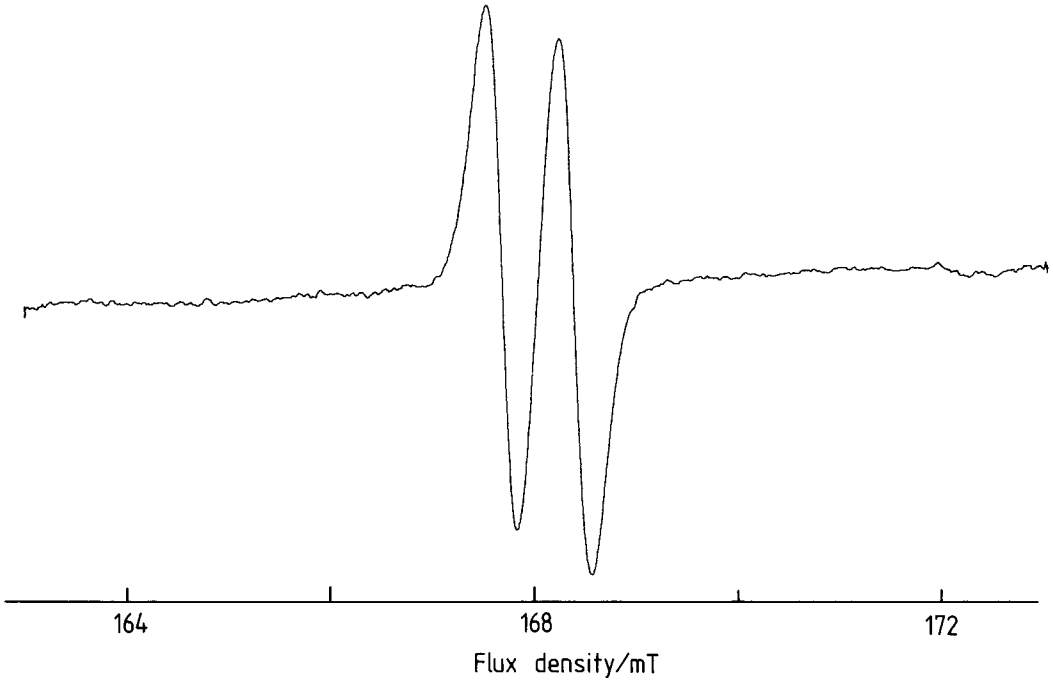

FIG. 2.—Far-infrared laser magnetic resonance spectrum associated with the $J = 1 \leftarrow 0$ transition of P^+ in its ground ^3P state, recorded with the 60.68 μm line of CH_3OH pumped by the $10R(52)$ line of a CO_2 laser. The spectrum was recorded with the oscillating magnetic field of the laser perpendicular to the applied magnetic field, inducing $\Delta M_J = \pm 1$ transitions. The output time constant of the lock-in amplifier was 0.3 s. The splitting arises from the ^{31}P nuclear hyperfine interactions ($I = \frac{1}{2}$).

pendent sources of error: first, the uncertainty in laser frequency as used in the experiment (1.5 MHz); second, the error in measurement of the flux density (0.05 mT); and third, the model error from the assumed value for $g_{J=1}$. The size of the last error can be estimated by using the very accurate, calculated value for g_J of ^{28}Si (1.501097, Veseth 1980) instead of the experimental value. This causes a shift of 0.72 MHz in the extrapolated zero-field frequency. The combined effect of these three uncertainties is 1.7 MHz. The uncertainty in the hyperfine parameter A_1 depends predominantly on the measurement uncertainty of the splitting between the two resonances. This is estimated to be 0.02 mT, leading to an uncertainty in A_1 of 0.4 MHz.

3. DISCUSSION

The $J = 1 \leftarrow 0$ fine-structure interval of P^+ ion in its ground ^3P state has been accurately measured to be 4944433.0 ± 1.7 MHz, a value that corresponds to a wavenumber of 164.92853 cm^{-1} or a wavelength of 60.63232 μm. This measurement is more than 800 MHz larger than the previously best available value, obtained indirectly from optical measurements (Martin et al. 1985); it is more than 2 orders of magnitude more accurate.

The ^{31}P nuclear hyperfine splitting has also been observed, apparently for the first time. This has allowed the determination of a single hyperfine parameter, A_1, which governs the splitting for P^+ in the $J = 1$ level. The value obtained, −28.6 MHz, is considerably larger than the value of −3.7 MHz obtained by simply scaling the corresponding value for the isoelectronic atom, ^{29}Si, in the ratio of the nuclear g-factors. This is a manifestation of the net charge on the atom, which draws the outermost electrons in more tightly so that the expectation value $\langle r_i^{-3} \rangle$ is increased.

It will be interesting to see whether the 60.6 μm transition of P^+ can be detected in appropriate ionizing regions of space. The present measurements allow the zero-field frequencies of the hyperfine components of the $J = 1 \leftarrow 0$ transition to be predicted with an accuracy of 1.7 MHz. The calculated frequencies are listed in Table 3.

This work has been supported in part by NASA contract W18-623.

TABLE 3

CALCULATED VALUES FOR THE ZERO-FIELD FREQUENCIES OF THE $J = 1 \leftarrow 0$ FINE-STRUCTURE TRANSITION IN $^{31}P^+$

Transition	ν (GHz)	Relative Intensity[a]
$J = 1 \leftarrow 0$:		
$F = \frac{1}{2} \leftarrow \frac{1}{2}$.....	4944.4622 (17)[b]	1.340
$F = 1\frac{1}{2} \leftarrow \frac{1}{2}$	4944.4180 (17)	2.679

[a] The relative intensity is given by the square of the magnetic dipole transition moment, $\langle LSJIF' \| (\boldsymbol{m}/\mu_B) \| LSJIF \rangle^2$.
[b] Estimated uncertainty (1 σ).

REFERENCES

Brown, J. M., Evenson, K. M., & Zink, L. R. 1993, Phys. Rev. A, 48, 3761
———. 1994a, ApJ, 431, L147
Brown, J. M., Varberg, T. D., Evenson, K. M., & Zink, L. R. 1994b, ApJ, 428, L37
Brown, J. M., Zink, L. R., & Evenson, K. M. 1994c, ApJ, 423, L151
Cooksy, A. L., Hovde, D. C., & Saykally, R. J. 1986, J. Chem. Phys., 84, 6101
Guélin, M., Cernicharo, J., Paubert, G., & Turner, B. E. 1990, A&A, 230, L9
Haas, M. R., Hollenbach, D. J., & Erickson, E. F. 1991, ApJ, 374, 555
Lugten, J. B., Genzel, R., Crawford, J. K., & Townes, C. H. 1986, ApJ, 306, 691
Martin, W. C., Zalubas, R., & Musgrove, A. 1985, J. Phys. Chem. Ref. Data, 14, 751
Moore, C. E. 1949, Atomic Energy Levels as Derived from the Analyses of Optical Spectra, Vol. 1 (Circ. Natl. Bur. Stand. 467) (Washington: NBS)
Svendenius, N., Magnusson, C. E., & Zetterberg, P. O. 1983, Phys. Scr., 27, 339
Tielens, A. G. G. M., & Hollenbach, D. J. 1985, ApJ, 291, 722
Turner, B. E., & Bally, J. 1987, ApJ, 321, L75
Varberg, T. D., Brown, J. M., & Evenson, K. M. 1994, J. Chem. Phys., 100, 2487
Vasconcellos, E. C. C., Zerbetto, S. C., Holecek, J. C., & Evenson, K. M. 1995, Opt. Lett., 20, 1
Veseth, L. 1980, Phys. Rev. A, 22, 803
Wright, E. L., et al. 1991, ApJ, 381, 200
Ziurys, L. M. 1987, ApJ, 321, L81