Laser-magnetic-resonance detection of magnesium atoms in the metastable $^3P_{0,1,2}$ states

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Transitions between fine-structure levels of the metastable ($3s3p^3P$) state of magnesium have been observed by means of the highly sensitive technique of far-infrared laser-magnetic-resonance spectroscopy. The g factors for the $^3P_1$ and $^3P_2$ levels are 1.50111(16) and 1.50102(16), respectively, and the $^3P_1$–$^3P_2$ energy separation is 1 220 575.1(33) MHz. The observed g factors show good agreement with the predicted values. This stands in marked contrast to similar results for atomic silicon (^3P) and aluminum (^2P), for which the theoretical and experimental g factors differ substantially. The value of the $^3P_1$–$^3P_2$ energy separation is improved by nearly 2 orders of magnitude over the optical value and is of sufficient accuracy to permit possible extraterrestrial identification.

INTRODUCTION

The technique of far-infrared (FIR) laser-magnetic-resonance (LMR) spectroscopy is a highly sensitive, high-resolution method for obtaining atomic and molecular spectra in the region between 40 and 1000 μm.[1] The high sensitivity, derived mainly from intracavity operation and high frequencies (compared with conventional microwave systems), places FIR LMR among the most sensitive absorption techniques available, with a minimum detection limit estimated to be of the order of 5×10^{-10} cm^{-1}.[2] As a result, LMR has been widely applied to the spectroscopic study of a large number of atoms, free radicals, and metastable molecules, yielding accurate transition frequencies, spectroscopic constants, and atomic and molecular g factors.

Accurate values for atomic g factors and fine-structure separations have traditionally provided critical tests for the theory of atomic structure, and although the level of understanding of atomic energy levels has reached a mature state, advances in high-resolution spectroscopic technology continue to provide challenges for theorists. With the LMR technique, for example, recent measurements of the fine-structure transitions in the ground ^3P states of atomic oxygen,[3] carbon,[4] and silicon[5] have yielded fine-structure splittings and g factors for the atomic levels involved. The most recent of these studies[5] has shown rather large differences (267×10^{-6}) between the theoretical and experimental g factors in Si(^3P), the origins of which do not appear firmly established. Even larger discrepancies have been reported for Al(^2P) (672×10^{-6}),[6,7] and calculations for many of the first-row elements as well as for Cl(^2P) and some of the alkali metals agree with experiment to better than 1 part in 10^5.[6] In general, the difference between theory and experiment for atomic g factors has been quite variable, and it appears that their *ab initio* calculation is not clear cut. In this context, then, additional data of this nature would seem useful, and we report here a similar study of the lowest metastable (^3P) state of magnesium. The high sensitivity and resolution obtainable by LMR has provided accurate g factors for both the $^3P_1$ and the $^3P_2$ well as an improved value for the $^3P_1$–$^3P_2$ separation.

The ^3P state of magnesium is of interest for a number of other reasons as well. The metastable is only weakly radiatively coupled to the ground ^1S state, with transitions from the $^3P_0$ and $^3P_2$ levels being rigorously forbidden. The decay of the $^3P_1$ state, however, is allowed owing to mixing with the $^1P_1$ state and occurs with a lifetime of the order of several milliseconds.[8] This long lifetime renders the metastable a chemical species in its own right and has permitted the study of a number of its energy-transfer and chemical reactions.[9] The interest in metastable magnesium for metrology was recognized in 1972 by Strumia,[10] who proposed it as a basis for an absolute submillimeter frequency standard. In his scheme, a natural state selection would be achieved in a metastable beam by preferential decay of the $^3P_1$ state, thus leaving only the $^3P_0$ and $^3P_2$ levels populated. The development of sources, signal-handling systems, and submillimeter technology has recently made possible the measurement of the $^3P_0$–$^3P_1$ transition at 601 277.160(4) MHz in an atomic beam, thus providing a basis for the experimental realization of the magnesium frequency standard.[11] The frequency of the $^3P_1$–$^3P_2$ transition, however, was inaccessible in those experiments and therefore remained known (from optical spectra) to roughly 100 MHz.[12] The improved value for the frequency of the $J = 1$–2 transition measured here thus provides a satisfying complement to the recent results of the atomic-beam study.

Finally, it is worth noting that in addition to the usual difficulties[3] associated with LMR studies of atoms (low spectral density and the magnetic-dipole nature of atomic fine-structure transitions), the study of Mg(^3P) has presented a number of further experimental challenges. In previous LMR studies of carbon, silicon, and oxygen, the absorbing species was readily produced from gaseous starting materials (CH_4, SiH_4, or O_2) containing the element, but no such volatile

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compounds exist for magnesium, which must therefore be produced by direct vaporization of the metal. Moreover, in contrast with the previous studies, the state under investigation in this work is not the ground state, and the metallic vapor, once produced, must be subjected to the proper conditions for formation of the metastable. Last, owing to the longer-wavelength operation required by the smaller fine-structure separations of (^3P) Mg, the corresponding transition probabilities are 600 and 60 times smaller than those for oxygen and silicon, respectively. Despite these difficulties, however, we have been able to observe both the $^3P_0$–$^3P_1$ and the $^3P_1$–$^3P_2$ transitions, thus further demonstrating the high sensitivity of the LMR technique.

EXPERIMENT

The FIR LMR spectrometer has been described in detail elsewhere.[1] Briefly, it consists of a FIR gain cell pumped transversely by a grating-tuned CO_2 laser and separated from the intracavity sample region by a polypropylene beam splitter mounted at Brewster's angle to the FIR cavity. The sample region is situated between the ring-shimmed Hyperco 38-cm pole caps of an electromagnet, producing a homogeneous field region 7.5 cm in diameter. The magnetic field is modulated at 13 kHz by a pair of Helmholtz coils, and the laser output is monitored with a liquid-helium-cooled In–Sb bolometer. The signal is demodulated by using a lock-in amplifier and is approximately equal to the first derivative of the absorption line.

Several different experimental configurations were tried to produce Mg(^3P) inside the laser cavity. The first successful experiment was performed with a hollow-cathode direct-current discharge, which was a miniaturized version of that described in Ref. 13 and was placed just outside the laser cavity. The discharge current, several tens of milliamperes, was sustained by argon and run almost collinearly with the magnetic field. Large cathode diameters could not be used, and the gas pressure could not be lower than about 40 Pa (1 Torr = 133 Pa). Under the proper conditions, in addition to a bright green emission produced in the hollow-cathode region, a deep blue emission (457.1 nm) resulting from the radiative decay of the $^3P_1$ level could be observed inside the laser cavity. Unfortunately, however, this configuration suffered from severe instability, especially at higher magnetic fields, and did not provide a reproducible source of the metastable state.

A stable source of Mg(^3P) consisted of a resistively heated titanium oven through which a steady flow of argon was maintained to entrain the metallic vapor. The total pressure was held between 80 and 133 Pa, and the magnesium atoms were excited to the metastable state before entering the laser cavity by a hot cathode discharge operated at about 3 mA. Special care was taken to mount the discharge electrodes at least 1 cm from the vacuum walls in order to eliminate arcing to a rapidly deposited magnesium layer. Under optimum operating conditions, the deep blue emission from the $^3P_1$ state filled the laser cavity, and little of the bright green emission could be observed.

RESULTS AND DISCUSSION

Table 1 lists the observed transitions and their assignments, and Fig. 1 presents a graphic summary. Figure 2 shows the $^3P_1$–$^3P_2$ transition as observed on the 1 236 396.8-MHz line of CH_3OH. The spectrum appears as a closely spaced, but well resolved, triplet owing to the M_J dependence of the quadratic Zeeman coefficients as indicated in the third term of Eq. (1) below. For a ^3P state, only the $\Delta M_J = \pm 1$ transitions are observable by LMR.

The observed spectra may be analyzed by using an energy-level expression of the form

$$W(J, M_J) = W_0(J) + \mu_B g_J M_J B + c(J, M_J)B^2, \quad (1)$$

where μ_B is the Bohr mageton, $W_0(J)$ is the zero-field energy of the ^3P_J state, g_J is the g factor for that state, and $c(J, M_J)$ are the second-order Zeeman coefficients, which have been given elsewhere.[4] The accurately measured[11] value of $\nu_{01} = W_0(1) - W_0(0)$ is constrained in our analysis, leaving $\nu_{12} = W_0(2) - W_0(1)$, g_1, and g_2 to be determined from the data. Since the primary sources of uncertainty in the determination of these quantities arise from that in the magnetic-field measurements, as well as from knowledge of the laser frequency (imposed by the resettability of the laser line to the center of the Doppler-broadened profile), the most accurate values are obtained from measurements having the largest Zeeman shifts, viz., transitions Ⓒ-Ⓗ in Table 1. In particular, as dictated by Eq. (1), the transitions Ⓔ and Ⓕ depend only on ν_{12} and g_1 and may therefore be used to obtain the values ν_{12} = 1 220 574.4(33) MHz and g_1 = 1.50111(16). Likewise, transitions Ⓒ and Ⓗ depend only on ν_{12} and g_2 and give ν_{12} = 1 220 575.7(33) MHz and g_2 = 1.50102(16). The determination of any of these parameters using any other combination of transitions in Table 1 results in values that are consistent with those given above but significantly less precise. We therefore report the values g_1 = 1.50111(16), g_2 = 1.50102(16), and ν_{12} = 1 220 575.1(33). Finally, we note that a determination of ν_{01} using transitions Ⓐ and Ⓑ yields the result ν_{01} = 601 276.9(20) MHz, which is in excellent agree-

Table 1. Observed Transitions of Mg(^3P)

J	M_J	J'	M_J'	$B(T)$	Laser Line[a]	λ (μm)	Lasing Gas	ν_L (MHz)
0	0	1	1	0.05265(2)	Ⓐ	497.7	CD_2F_2	602 383.9(2)
0	0	1	−1	0.11355(2)	Ⓑ	500.6	CD_2F_2	598 893.7(2)
1	0	2	−1	0.58167(5)	Ⓒ	248.1	CD_2F_2	1 208 313.9(4)
1	−1	2	−2	0.58424(5)	Ⓓ	248.1	CD_2F_2	1 208 313.9(4)
1	1	2	0	0.58509(5)	Ⓔ	248.1	CD_2F_2	1 208 313.9(4)
1	−1	2	0	0.75059(6)	Ⓕ	242.5	CH_3OH	1 236 396.8(4)
1	1	2	2	0.75199(6)	Ⓖ	242.5	CH_3OH	1 236 396.8(4)
1	0	2	1	0.75645(6)	Ⓗ	242.5	CH_3OH	1 236 396.8(4)

[a] Fig. 1.

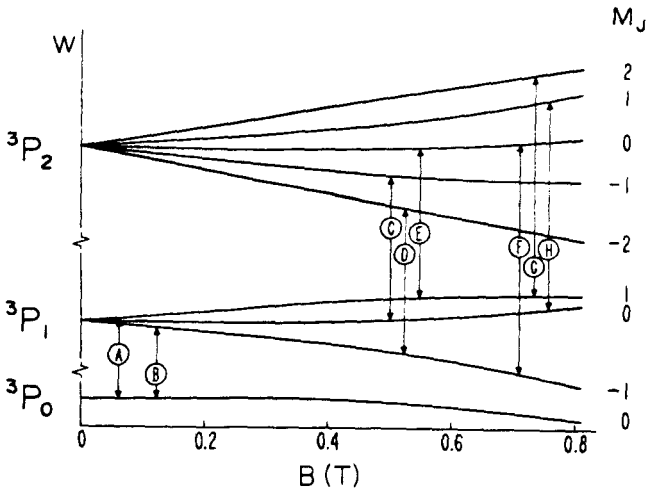

Fig. 1. Energy-level diagram for Mg(^3P) showing observed transitions. The second-order Zeeman effect has been exaggerated for clarity.

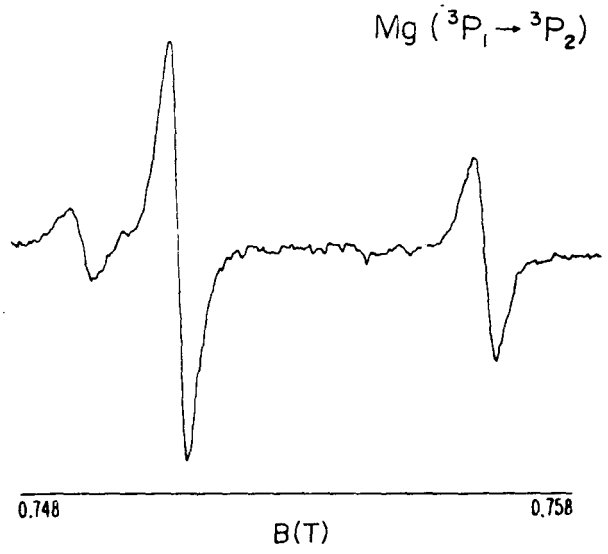

Fig. 2. The $^3P_1$–$^3P_2$ transition of magnesium as observed on the 1 236 396.8-MHz line of CH_3OH.

Table 2. Comparison of Present Results with Previous Work

	This Work	Previous Work
ν_{01} (MHz)	601 276.9(22)	601 277.160(4)[a]
ν_{12} (MHz)	1 220 575.1(33)	1 220 600[b]
g_1	1.50111(16)	1.501158[c]
g_2	1.50102(16)	1.501160[c]

[a] Ref. 11.
[b] Ref. 12.
[c] Calculated value; Refs. 14 and 15.

ment with the more accurate result of the atomic-beam work. This agreement provides evidence that the primary sources of uncertainty in the reported measurements are indeed due to uncertainties in the magnetic-field and laser-frequency measurements used in the Zeeman extrapolation and that the reported values are, to within the estimated uncertainty, free of environmental effects.

Table 2 presents the results of this work and compares them with the previous experimental and theoretical values. The value of ν_{12} is seen to be in good agreement with that from optical data but is significantly more accurate. To within the experimental uncertainty, it is seen that $g_1 = g_2$, and the values obtained are in good agreement with the predicted values.[14,15] Evidently, the differences between experiment and theory are smaller for magnesium than are those reported for silicon and aluminum, although an accurate check of the calculated values is not possible with the existing experimental uncertainty. The results, however, are at least consistent with the expectation that singlet–triplet mixing should lower g_1 by only 2×10^{-6} and that the relativistic and diagmagnetic contribution to g_1 and g_2 should be of the same order of magnitude. It is unfortunate that the measurements do not permit six-decimal-place accuracy, from which these effects could be more closely scrutinized.

Finally, we note that the accurate fine-structure intervals for Mg(^3P) now available from this work as well as that of Ref. 11 provide another possible means by which to study this species in the interstellar medium. Optical emissions from Mg(^3P) have been observed in planetary nebulae,[16] and the intensity ratios found are strongly suggestive of anomolous population ratios for these levels. Moreover, the metastable triplet could be excited by particle bombardment, generating spectra in both the visible and the FIR. In this case, the mechanism of excitation is different from the hydrogen-atom collisions assumed to be responsible for the observation of atomic fine-structure transitions from ground-state atoms[17] and thus may permit the study of new atomic processes in the interstellar medium.

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