$R/(1-R) \sim 10^2$ (typically). The infrared Q values of McGroddy, McAlister, and Stern for gold have too large error bars for real comparison even as to sign, but are not inconsistent with our q magnitudes. Of course, existing magnetoreflectivity data are for $T \leq 300°K$, and a slight decrease would be expected at 1000°C.

[4]S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instr. 40, 761 (1969); J. C. Kemp, J. Opt. Soc. Am. 59, 950 (1969).

[5]A. H. Wilson, *Theory of Metals* (Cambridge Univ., Cambridge, England, 1936), p. 123; F. Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 638.

[6]A free-electron bremsstrahlung model in Ref. 1 gives $q = 4\Omega/\omega$ in an appropriate limit. But that is for an almost transparent system, without skin effects. The magnetoabsorption fraction through an almost transparent metal film with a Drude magnetoconductivity $\sigma_{\pm} = \sigma_0[1 + i\tau(\omega \mp 2\Omega)]^{-1}$ is $-4\Omega/\omega$, to first order in Ω and for $\omega\tau \gg 1$, and the corresponding q is the same. The factor 4 reduction in an opaque metal body is an aspect of internal radiative transfer, which tends to make the radiation more blackbodylike and less polarized (see Ref. 1); yet the effect survives if $\omega < \omega_p$, which means the surface is appreciably reflective. [Another but quite unrelated factor of 4 appears in comparing free-electron versus bound-electron models (see Ref. 1), in both cases for almost transparent bodies: In an opaque bound-electron system, again with $\omega < \omega_p$, the magnetoemissivity would by extension be $-\Omega/(4\omega)$, or in any case less than the first term in Eq. (1).]

[7]Anomalous skin-depth effects can also be involved in such variations, as with ordinary surface absorption in the near infrared; see H. E. Bennett, J. M. Bennett, E. J. Ashley, and R. J. Motyka, Phys. Rev. 165, 755 (1968).

[8]A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, London, 1948), pp. 22 and 44, and *The Spectroscopy of Flames*, Wiley, New York, 1957), p. 114.

MAGNETIC RESONANCE OF SOME OPTICALLY ORIENTED EXCITED IONS OF Zn AND Cd

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Using the strong spin dependence of large cross-section Penning reactions between He($^3S_1$) atoms and group-II metal atoms, it is shown that optical pumping can be extended to the excited states of ions. Magnetic resonance is observed for Cd^+ $5^2D_{5/2}$ and Zn^+ $4^2D_{3/2}$ and $4^2D_{5/2}$ excited ion levels. The measured lifetimes of these levels are 0.773 $\pm$0.027, 2.22 $\pm$0.11, and 1.61 $\pm$0.10 μsec, respectively.

This Letter reports the extension of optical pumping techniques to the observation of magnetic resonances in the excited states of ions by utilizing the strong spin dependence of Penning reactions between metastable (^3S) helium atoms and group-II metal atoms. In particular we have observed magnetic resonances of Zn^+ ions in the $4^2D_{3/2}$ and $4^2D_{5/2}$ levels and Cd^+ ions in the $5^2D_{5/2}$ level. From the measured resonance linewidths we have determined the radiative decay times of these levels, and we are able to place an upper limit on the magnitude of the collisional mixing cross section.

Cross sections for Penning reactions between metastable helium atoms and impurity atoms are known to be large.[1] Consequently, this is an attractive reaction for producing large densities of impurity ions; indeed, Silfvast has constructed various laser sources utilizing Cd, Zn, and Sn as the impurity atom.[2,3] Further, it was demonstrated earlier that if the metastable helium atoms are initially spin polarized by optical pumping, the polarization is very effectively transferred to the impurity ions.[4] The transfer of polarization from optically oriented metastable (^3S) helium atoms to excited states of ions of Cd, Zn, Hg, Mg, Ca, Sr, and Ba has been observed by monitoring the polarization of the optical emission when the excited ion decays.[4] We have also detected the polarization of the ground-state ions of Ca, Sr, and Ba by monitoring the absorption of circularly polarized ion resonance radiation. We report here the observation of magnetic resonances in some excited states of Cd^+ and Zn^+ ions.

The experimental apparatus used in this experiment is described in Ref. 4. It consists principally of a flowing helium afterglow and a local oven containing small amounts of either Zn or Cd metal. Provision is made to optically pump the metastable ($^3S_1$) helium atoms in the flow prior to the Penning collisions with the impurity-metal atom. The flow system is situated in an external magnetic field so that the flow is perpendicular to the field direction. The metastable helium density determined by optical absorption

of 1.08-μm resonance radiation is about 8×10^{10} cm^{-3} with a flow velocity of 2×10^{3} cm sec^{-1}. The total pressure is between 0.2 and 0.6 Torr. The metal is heated until the helium metastable density is reduced by 50% as a result of Penning collisions with the free metal atoms. This implies an ion density of about 4×10^{10} cm^{-3} which is confirmed by optical absorption of ion resonance radiation.

In the Penning reaction with the 19.78-eV metastable helium atoms, ions are created in a number of excited states; the excess energy is carried off by the Penning electron. For Zn, a possible reaction is

$$He(2^3S_1) + Zn(^1S_0) \rightarrow He(^1S_0) + Zn^+(4^2D_{3/2}) + e, \quad (1)$$

followed by

$$Zn^+(4^2D_{3/2}) \rightarrow Zn^+(4^2P_{1/2}) + h\nu(5894\ \text{Å}). \quad (2)$$

The helium metastable atoms are initially spin polarized by optical pumping, and the polarization is very efficiently transferred to the Zn^+. As the polarized Zn^+ $4^2D_{3/2}$ ions decay with emission at 5894 Å, the polarization of the ions is detected by monitoring the polarization of the emitted radiation. In the experiment we examine the intensity of the two circularly polarized components (σ^+ and σ^-) emitted in the magnetic field direction. Defining the ion polarization in the usual fashion,

$$P = (\sigma^+ - \sigma^-)/(\sigma^+ + \sigma^-),$$

we measure $P \sim 20\%$. One can destroy the ion polarization by application of an rf magnetic field at the resonance frequency of either the metsastable helium atoms ($g = 2$) or the $Zn^+(^2D_{3/2})$ ions. In the first case we are observing the magnetic resonance of the helium metastable atoms at $g = 2$, while in the second case we observe the magnetic resonance of the $^2D_{3/2}$ level with $g_J = 0.8$.

In our experiment an oscillating magnetic field at 9.60 MHz is applied perpendicular to the external magnetic field and parallel to the flow direction, while the external magnetic field is scanned slowly through the resonance condition. The optical radiation from the emitting ions is viewed along the field direction through a rotating quarter-wave plate and linear polarizer. Thus, we alternately sample the σ^+ and σ^- ion radiation. The circularly analyzed light is incident on the slits of a $\frac{1}{4}$-m Bausch and Lomb monochromator for wavelength selection and then detected with a photomultiplier. The output of the photocell is synchronously detected with a lock-in amplifier at twice the frequency of rotation of the quarter-wave plate.

Figure 1 is a recording of the lock-in output as the magnetic field is scanned through the resonance condition of the $Zn^+(4^2D_{3/2})$ ions at $g = 0.8$. A resonance (not shown) also appears at $g = 2$, corresponding to a saturation of the metastable helium polarization. Similar resonances at $g_J = 1.2$ with differing widths are observed for the $Zn^+(4^2D_{5/2})$ and the $Cd^+(5^2D_{5/2})$. The natural metal was used in each case and the results reported are for the even isotopes. For Cd, 25% of the natural metal is of the odd isotopes for which the nuclear spin is $I = \frac{1}{2}$. The presence of the nuclear spin splits the $^2D_{5/2}$ level into the two hyperfine components $F = 3$, for which $g_F = 1$, and $F = 2$, with $g_F = 1.4$. The resonance at $g = 1$ due to the $F = 3$ level, however, is obscured by the saturation of the helium metastable atom polarization due to double-quantum transitions. The resonance at $g_F = 1.4$ was too weak to be observed with the available signal-to-noise ratio.

Contributions to the measured linewidth due to rf field broadening are removed by plotting the square of the linewidth as a function of the square of the rf-field intensity as shown in Fig. 2 and extrapolating the resulting straight line to zero field ($H_1 \rightarrow 0$) to yield the unperturbed linewidth. The width of the resonance at half-height in frequency units is obtained by measuring the displacement of the resonance line produced by a known change in the resonance frequency.

The extrapolated ($H_1 = 0$) linewidth is produced by (1) the radiative lifetime of the state, (2) collision-induced relaxation, and (3) field inhomogenieties over the sample volume. Contributions to the linewidth due to field gradients can be determined by monitoring directly the metastable helium resonance at $g = 2$. The maximum field inho-

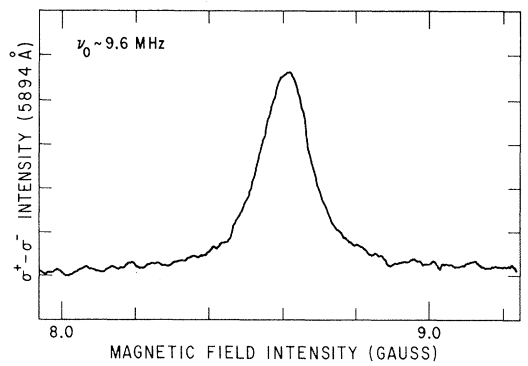

FIG. 1. Change in polarization of emitted $Zn^+(4^2D_{3/2}$-$4^2P_{1/2})$ as a function of applied external magnetic field.

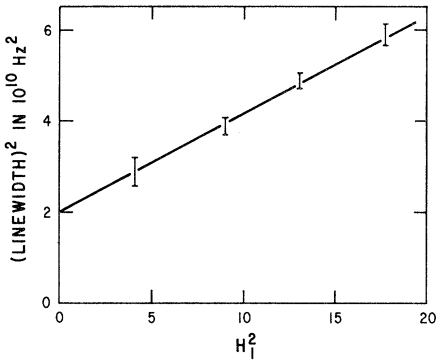

FIG. 2. The square of the measured linewidth as a function of rf field strength squared. Extrapolation to zero field strength yields the radiative decay rate. Curve shown is for the $^2D_{3/2}$ Zn^+ level.

mogeneity over the optically pumped volume is on the order of 3 mG. However, the field gradient experienced by the excited ion is much smaller than this since the displacement of the ion during its brief lifetime is small and the optical system used for detection samples but a small fraction of this optically pumped volume. Consequently, field inhomogeneities are negligible.

Collision-induced relaxation of the excited ion can also contribute to the observed resonance linewidths. The only species present in sufficient abundance to produce an effect are the ground-state helium atoms. The de-excitation rate for excited-ion–helium collisions is quite probably small since the ion energy levels are well separated and large amounts of kinetic energy would have to be exchanged. However, the cross section for collisional mixing among the m_J levels of the excited ion may be large.[5] The presence of mixing collisions would result in a pressure-dependent resonance linewidth. To investigate this possibility the resonance linewidths were measured as a function of pressure over the range 0.2-0.6 Torr. The measured linewidths were independent of pressure over this range within the experimental accuracy. In the absence of collision-induced relaxation the resonance linewidth in frequency units is then simply related to the radiative lifetime of the level:

$$\Delta\nu = (\pi\tau)^{-1}.$$

Table I summarizes the results obtained. Our measured lifetimes for Cd^+ agree well with the previously reported values. However, the $Zn^+(^2D_{3/2})$ lifetime reported here is about 5 times greater than that reported in Ref. 8. We believe the discrepancy to be due to a miscalculation since comparison of Figs. 18 and 19 of Ref. 8 would indicate a $Zn^+(4^2D_{3/2})$ lifetime substantially longer than for $Cd^+(5^2D_{5/2})$. On physical grounds one would also expect the Zn^+ lifetime to be longer than Cd^+.

If the entire uncertainty in the measurement of the decay time is attributed to collisional mixing over the pressure range 0.2-0.6 Torr, we can calculate an upper limit on the magnitude of the mixing cross section. We find then that $\sigma(\text{mix}) \leq 2\times10^{-17}$ cm^2 for the Zn^+ levels and $\sigma(\text{mix}) \leq 4\times10^{-17}$ cm^2 for the Cd^+ level. The small collisional mixing cross section is somewhat surprising in view of cross sections obtained in other systems involving non-S-state atoms which are more nearly equal to gas-kinetic cross sections. We wish to point out, however, that the electron configuration of the states investigated here is of the type $nd^9(n+1)s^2$. The outer electrons are in s orbitals and are apparently effective in shielding the core electrons from perturbations resulting from collisions. A similar explanation has been invoked for $He(1s^2)$-$Ne(2p^5 3s)$ collisions to account for the relatively small depolarization cross section of 4×10^{-17} cm^2 observed there.[9] The method utilized here to observe magnetic resonances in the ground or excited states of ions is potentially applicable to many levels of ions which are accessible energetically by Penning reactions with optically oriented metastable helium atoms and which simultaneously obey the

Table I. Results of lifetime measurements.

Ion	Level	Radiative decay time (this expt) (10^{-6} sec)	Radiative decay time (other expt) (10^{-6} sec)
Cd^+	$5^2D_{5/2}$	0.773 ± 0.027	0.670 ± 0.35[a] 0.783 ± 0.011[b] 0.83 ± 0.07[c]
Zn^+	$4^2D_{5/2}$	1.61 ± 0.11	...
Zn^+	$4^2D_{3/2}$	2.22 ± 0.11	0.465 ± 0.02[c]

[a] Ref. 6. [b] Ref. 7. [c] Ref. 8.

Wigner spin rule.

We wish to acknowledge the very capable assistance of F. D. Sinclair.

[1]The Penning cross section for He(2^3S)-Cd collisions is $(4.5 \pm 0.2) \times 10^{-15}$ cm^2 [L. D. Schearer and F. A. Padovani, J. Chem. Phys. 52, 1618 (1970)]; the cross section for He(2^3S)-Zn is 1.6×10^{-15} cm^2 (to be published).

[2]W. T. Silfvast, Appl. Phys. Letters 13, 169 (1968).

[3]W. T. Silfvast, Appl. Phys. Letters 15, 23 (1969).

[4]L. D. Schearer, Phys. Rev. Letters 22, 629 (1969).

[5]A. Dienes and T. P. Sonowski (private communication, and to be published) recently obtained a collisional mixing cross section for the $Cd^+(5^2D_{5/2})$-He($^1S_0$) system of 6.1×10^{-16} cm^2 by measuring the width of the zero-magnetic-field dip for the 4416-Å transition of the He-Cd laser as a function of pressure. There is considerable uncertainity in this measurement, however, since the width of the power dip is also very sensitive to changes in the electron-Cd^+ collision frequency.

[6]M. B. Klein, to be published.

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DIRECT DISTORTION OF ELECTRONIC CLOUDS OF RARE-GAS ATOMS IN INTENSE ELECTRIC FIELDS

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Self-phase modulation originating from a direct distortion of the atomic electronic charge density has been observed in liquid argon and liquid and solid krypton.

Self-phase modulation (SPM) and small-scale filaments originating from a direct electronic distortion of rare-gas atoms have been observed in liquid argon and liquid and solid krypton. This experimentally demonstrates that significant changes in the atomic shape take place under the action of the radiation pressure from the intense electric fields of picosecond light pulses.

Self-phase modulation was first observed[1] in liquid CS_2 and attributed to the orientational Kerr effect of CS_2 molecules and later to a rocking mechanism.[2] Molecular electronic distortion[3] has been shown to lead to self-trapping in centrosymmetric molecules. Recently SPM was observed in crystals and glasses[4] due to either direct distortion of electronic clouds around nuclei or one of several coupled electronic mechanisms: librational distortion where electronic structure is distorted as the molecule rocks, electron-lattice distortion where the electron cloud distorts as the lattice vibrates, and molecular redistribution where electronic shells are altered as the nuclei redistribute spatially.

Rare-gas liquids are composed of atoms possessing spherical symmetry. Thus there are no orientational, librational, or electron-lattice contributions to the nonlinear refractive index coefficient n_2. Contributions to the nonlinear refractive index might be expected from electrostriction, molecular redistribution, and a direct distortion of the electron clouds. Electrostriction is ruled out because picosecond exciting pulses are too short. Molecular redistribution[5] arises from fluctuations in the local positional arrangement of molecules and can contribute significantly to n_2. However, we estimate[6] n_2 due to all mechanisms except electronic to be 1×10^{-14} esu for liquid argon from depolarized inelastic-scattering data.[7] Electronic distortion ($n_2 = 0.6 \times 10^{-13}$ esu) dominates all nonlinear index contributions. Furthermore, the depolarized inelastic light scattering wing vanishes in solid xenon,[8] implying that the molecular redistribution contribution to n_2 vanishes in rare-gas solids. Observation of self-focusing and SPM in rare-gas liquids and solids appears to provide a direct proof that atomic electronic shells are distorted from their spherical symmetry under the action of the applied field.

Experimentally a Nd glass mode-locked laser is used to generate picosecond light pulses which are then converted in a potassium dihydrogen phosphate crystal to second harmonic pulses at 5300 Å. Second harmonic pulses of power ~$(2.5$-$8) \times 10^8$ W are focused with a 25-cm focal length lens into 12-cm-long samples of argon and krypton. The beam intensity in the liquids is ~4×10^{11} W/cm^2 over a beam waist length of ~7 cm. The beam diameter is photographically measured to be 300 μm at the focal point and 400 μm at 3.5 cm to both sides from the focal distance. A collimated beam of diameter 1.1 mm could not pro-