

VIII International Quantum Electronics Conference

SESSION A

Monday, June 10, 1974 8:30 A.M.-12:06 P.M.

Tunable Lasers and Spectroscopy

A.1 The Laser Revolution in Chemistry
(Invited), R. N. Zare, Dept. of Chemistry,
Columbia University, New York, N.Y.

A.2 Selective Excitation, Photoionization and Isotope Analysis with High Power Tunable Dye Lasers, D. J. Bradley, C. H. Dugan, P. Ewart and A. F. Purdie, *Physics Department, Imperial College, London SW7 2BZ.*

Absorption spectroscopy of excited atomic levels allows the study of transitions to levels not reached from the ground state, as well as to autoionizing levels. The spectra are recorded in the visible and near ultra-violet spectral regions so that vacuum ultraviolet techniques are not required. Significant populations of excited states can now be obtained by selective excitation with high power, tunable dye lasers (1, 2), and new absorption spectra, series perturbations, photoionization and autoionization have been observed experimentally (3, 4, 5). In particular the strong autoionizing transition to the previously unobserved $3p^2 \ ^1S_0$ level of Mg I has been recorded at λ 300.9nm in good agreement with theory (5). Photoionization from excited states is an important process in stellar atmospheres where such transitions and dielectronic recombination will be factors in determining the ultra-violet radiation balance. The work reported here was designed to measure the cross-section for this $3s3p \ ^1P_1 - 3p^2 \ ^1S_0$ transition in Mg I at λ 300.9nm. The techniques developed can also be used for selective isotope separation.

A high power, frequency tunable dye laser, described in earlier publications (3, 6), provides a resonance light pulse at λ 285.2nm. This pulse is of sufficient power to saturate an optically thin vapour of Mg I over the length of a cylin-

drical electrode assembly placed inside a metal vapour oven. Under conditions of saturation pumping the atom density of the vapour gives a measure of the population of the $3s3p \ ^1P_1$ state. A second, simultaneously pumped, dye laser provides a high power photoionizing pulse at λ 300.9nm which passes through the excited metal atoms. The resulting photoelectrons are directly collected on an electrode. Guard electrodes are employed to ensure that the recorded photoelectron current comes from a known volume of the excited vapour. The measured current value, displayed on a fast risetime oscilloscope, then leads to the photoionization cross-section.

A similar technique can be used to detect photoionization from selectively excited states in alkali metals. A beam of atomic sodium directed through a flash photolysis cell is selectively excited by a pulse from a flashlamp pumped dye laser. The exciting radiation passes transversely through the atomic beam inside the cell, and is synchronized with the firing of the photolysing flashlamps. The photon energies of the flashlamps restricts photoionization to only those atoms which have been excited to the $^2P_{3/2,1/2}$ states. The photoelectrons are collected by an electrode system running parallel to the atomic beam. For lithium this method permits the selective ionization of one isotope by tuning the exciting laser across the resonance lines of Li^6 and Li^7 .

A.3 OH Spectroscopy Using an Intense Tunable UV Laser Beam, Charles C. Wang and L. I. Davis, Jr., *Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121*

This paper is intended to review the results of our experiments performed during the past year and experiments currently undertaken on the spectroscopic properties of hydroxyl (OH) radicals in the atmosphere and in a flame. The experiments were performed with an intense tunable laser beam in the ultraviolet with 0.4 cm^{-1} spectral width, $0.5 \mu\text{sec}$ duration, and up to 6 mJ energy per pulse. With this powerful tunable source in the ultraviolet, we have been able to obtain measurements hitherto unattainable. Most notable among them are (1) measurement of OH concentration in air down to 10^6 OH/cm^3 level; (2) observation of two-photon absorption of water leading to generation of OH as a dissociation product, and the identification of the 1A_2 state of water; (3) direct measurement of the population distribution in the ground electronic state of OH; and (4) the use of two-photon dissociation of water as a new OH

source for studying the rates of electronic quenching under atmospheric conditions.

It has been recognized for some time that OH plays a central role in smog formation and in controlling the global concentrations of carbon monoxide and methane.¹ However, the ambient OH was not detected until recently.² This ability to measure ambient concentrations of OH should afford an accurate determination of numerous photochemical cycles operative in either polluted or natural atmosphere. In this paper, the diurnal variation of OH concentration in an open atmosphere will be presented, and factors determining the detection limit discussed.

With a tightly focused beam, it is possible to generate OH in air by two-photon dissociation of water. Preliminary results indicate that dissociation takes place at least partly from the 1A_2 excited state of water. This excited state does not couple with the ground electronic state in electric dipolar transitions and has never been seen experimentally. Its location is a matter of high interest to molecular theorists. We are currently measuring the two-photon absorption cross section of water as a function of wavelength, and expect to map out the location of this excited state.

We have measured the population distribution and temperature of OH in the ground electronic state. This is done by tuning our laser to various rotational-electronic transitions of OH and detecting the fluorescence from the excited states. This technique provides spatial, temporal and spectral resolutions which are not possible with any conventional source, and as such it should prove particularly valuable in studying the dynamics of combustion.

Finally, the OH generated by two-photon dissociation of water has been used most conveniently as a source for studying the electronic quenching rates of excited OH under atmospheric conditions. Good results for nitrogen and water molecules have already been obtained. We are currently continuing this type of measurements for helium and other molecules. With our laser modified to provide shorter duration pulses, we also expect to study for the first time the temporal dependence of OH fluorescence.

¹For a comprehensive review, see, for example, H. Niki, E. E. Daby, and B. Weinstock, *Advances in Chemistry Series*, vol. 112, p. 16, 1972.

²C. C. Wang, *Bull. Am. Phys. Soc.*, vol. 19, paper AJ-1, February, 1974.

A.4 Balloon Borne Spin Flip Raman Laser Measurements of Stratospheric NO and H₂O
(Invited), C. K. N. Patel, *Bell Laboratories, Holmdel, N.J.*

¹T. J. McIlrath, *App. Phys. Lett.* vol. 15, p. 41, 1969.

²D. J. Bradley, G. M. Gale, and P. D. Smith, *J. Phys. B. Atom. Molec. Phys.* vol. 3, p. L11, 1970.

³D. J. Bradley, P. Ewart, J. V. Nicholas, and J. R. D. Shaw, *J. Phys. B. Atom. Molec. Phys.*, vol. 6, p. 1594, 1973.

⁴R. V. Ambartzumian and V. S. Letokhov, *Applied Optics*, vol. 11, p. 354, 1972.

⁵D. J. Bradley, P. Ewart, J. V. Nicholas, J. R. D. Shaw, and D. G. Thompson, *Phys. Rev. Lett.*, vol. 31, p. 263, 1973.

⁶D. J. Bradley, J. V. Nicholas, and J. R. D. Shaw, *App. Phys. Lett.*, vol. 19, p. 172, 1971.