NONLINEAR OPTICS AND LASER SPECTROSCOPY IN THE VACUUM ULTRAVIOLET

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1. INTRODUCTION

Over the past ten years enormous strides have been made towards producing novel sources of VUV and XUV radiation using lasers. This work has been motivated by many factors, including studies of highly-excited atomic states; interest in nonlinear optical phenomena; the development of x-ray lasers; and, the long-term prospect of applications of high energy radiation to photolithography in the production of integrated circuits. The spectroscopy community and, particularly, those in molecular spectroscopy, have been less active in fully exploiting the level of sophistication now available using laser techniques for studies of excited states in the VUV and XUV spectral regions. First, we now have the capability of producing high intensity [1-7], continuously-tunable, coherent and narrow line width VUV radiation, spanning the 100 nm - 200 nm region, with laboratory-scale dye laser systems. The intensity attainable [2,3] in the VUV ranges up to 10 kW per pulse (determined by the available dye laser system); in units of photons per 0.1 nm per second this intensity is \( \sim 8 \times 10^{17} \), or approximately 10⁷ times greater than that obtained following dispersion of currently available sources [8] of synchrotron radiation. Second, by using a sequence of harmonic generation steps or higher-order (≥ third-order) nonlinear processes, coherent radiation has been produced at wavelengths [9] as short as 38 nm. More recently, this work has been extended, using dye lasers, to produce tunable radiation in the 60-80 nm spectral region. Third, there is the pioneering work of Harris [11], in which anti-Stokes scattering from metastable species is used to convert visible-wavelength lasers to wavelengths as short as 20 nm. And, finally, there is a wide repertoire of nonlinear laser methods for...
studies of the spectroscopy and dynamics of excited states in the VUV: These include multiphoton absorption, multiphoton ionization [12,13], harmonic generation [14-16] and laser-assisted energy transfer [17]. All of these techniques will be discussed more fully below.

The above list does not highlight the use of actual VUV lasers because it was prepared from the perspective of molecular spectroscopy and dynamics, where narrow linewidths, time resolution and continuous tunability are the most important factors. Thus, although the first report [18] of the molecular hydrogen laser was the beginning of the rapid and successful development of VUV lasers, such devices have not found a wide range of applicability in spectroscopy. This is principally a result of either (i), an intrinsic lack of continuous tunability, as in the H₂ laser; or (ii), the difficulty in achieving suitably narrow linewidths, as in the excimer lasers.

This review discusses laser sources in the VUV in a broad context. First, we briefly review VUV lasers. The next section then deals with third-order nonlinear optical methods for producing tunable, coherent VUV radiation. A short discussion of anti-Stokes Raman effects is also included. Finally, we outline some examples of the application of tunable VUV laser sources to spectroscopy and molecular dynamics.

2. VACUUM ULTRAVIOLET LASERS

VUV lasers fall into two categories: First, there are the low-pressure, gas-discharge type lasers which use small molecules such as CO, H₂, HD or D₂ and in which the laser emission is between rovibronic levels of two bound potential energy surfaces. These levels are excited in a travelling-wave configuration (Blumlein), where the optical emission closely follows the excitation pulse, as the latter propagates through the laser medium, so that no optical cavity is required. In such lasers there is, therefore, no phase coherence in the output, which should be correctly classified as amplified spontaneous emission. Performance and other relevant parameters are summarized in Table 1.

The second category, the excimer lasers of the rare gases, uses an optical cavity. Excitation is either by an electron-beam pump to produce excimers [19] (Xe₂*, Kr₂*, Ar₂*) or by a high-pressure preionized discharge to generate exciplexes (ArF*) as the upper laser level. The laser transition is then a bound-continuum transition as indicated in Fig. 1. The observed con-