

CONF-92-211

Received by OSTI

DEC 1 1992

PNL-SA--21405

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October 1992

Presented at the
Advanced Laser Technology
for Chemical Measurements
October 19-21, 1992
Santa Fe, New Mexico

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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HIGH RESOLUTION STUDIES OF ATOMS AND SMALL MOLECULES*

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ABSTRACT

High resolution, continuous wave lasers have been utilized successfully in studies of small molecules. Examples of two-photon excitation schemes and of multiple resonance excitation sequences will be discussed within the framework of the spectroscopy and dynamics of selected Rydberg states of nitric oxide. Initial results on the circular dichroism of angular distributions in photoelectron spectra of individual hyperfine states of cesium will also be discussed.

INTRODUCTION

Historically, this research effort has focused on investigations of basic photophysical properties of atomic species with the principal objectives being to understand and to develop new approaches for ultratrace isotopic analysis. These studies have culminated in the technique of continuous-wave double resonance ionization mass spectrometry (cw-DRIMS). Knowledge of isotope shifts, hyperfine structure splittings, and decay channels have defined quantum state specific photoionization pathways affording highly selective and extremely sensitive analytical technologies applicable to rare radionuclides and toxic heavy metals within real environmental samples.

Comprehensive studies have recently been initiated to address the potential of analytical methodologies similar to cw-DRIMS to small molecules. Radicals that are components of the atmosphere and that are representative fragments generated during photodissociation of large molecules are of particular interest. The explicit purposes of these investigations are to provide detailed descriptions (*i*) of the dynamics of molecular photoionization, and (*ii*) of fundamental physical interactions involving electron spin and nuclear spin angular momenta and of the effects that these spin interactions exert upon the structural and dynamical properties of molecular excited states.

RESULTS AND DISCUSSION

The applicability of high resolution, continuous-wave laser sources to studies of small

* This research was supported by the U. S. Department of Energy, Office of Health and Environmental Research, under contract DE-AC06-76RLO 1830.

molecules has been demonstrated through initial investigations of the prototypical radical nitric oxide (NO). Doppler-free, two-photon fluorescence excitation spectroscopy has been used to catalog 351 rotational transitions within the $A-X(1,0)$ band¹ and to probe electron spin and nuclear spin interactions within selected rotational levels of the $(3s\sigma)A^2\Sigma^+(\nu=1)$ Rydberg state of $^{14}\text{N}^{16}\text{O}$.² The fine structure and hyperfine structure parameters characterizing this state have been extracted from these measurements. The effective cross section for two-photon excitation of $R_{11}(J''=2.5)$ is estimated to be $1 \times 10^{-44}\text{cm}^4\text{s}$.

High resolution $(2+1')$ optical-optical double resonance laser induced fluorescence (LIF) dip techniques have been used to determine the term energies and natural linewidths of individual rovibronic levels in the region of the $(4p\pi)K^2\Pi(\nu=2)$ and $(3d\delta)F^2\Delta(\nu=3)$ Rydberg states of $^{14}\text{N}^{16}\text{O}$. The observed term energies (Fig. 1) yield evidence for weak, mutual perturbations for both e and f symmetry components of the K ($\nu=2$) and F ($\nu=3$) rotational levels near $J=10.5-13.5$. The observed natural linewidths (Fig.2), which correspond

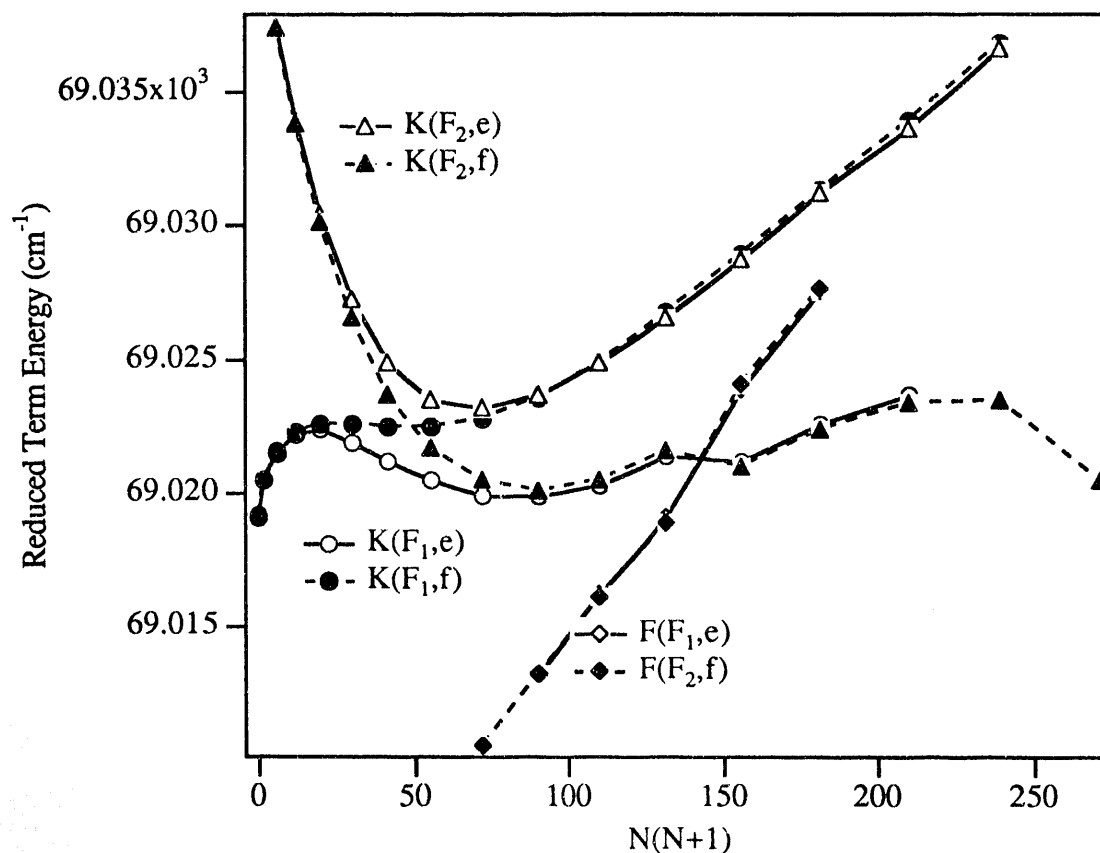


Figure 1. Reduced term energies as a function of $N(N+1)$ for e and f rotational levels of the $(4p\pi)K^2\Pi(\nu=2)$ and $(3d\delta)F^2\Delta(\nu=3)$ Rydberg states of $^{14}\text{N}^{16}\text{O}$.

to excited state lifetimes of the order of 500 picoseconds, dramatically confirm the existence of these mutual perturbations and provide evidence for the presence of more complex multistate interactions.

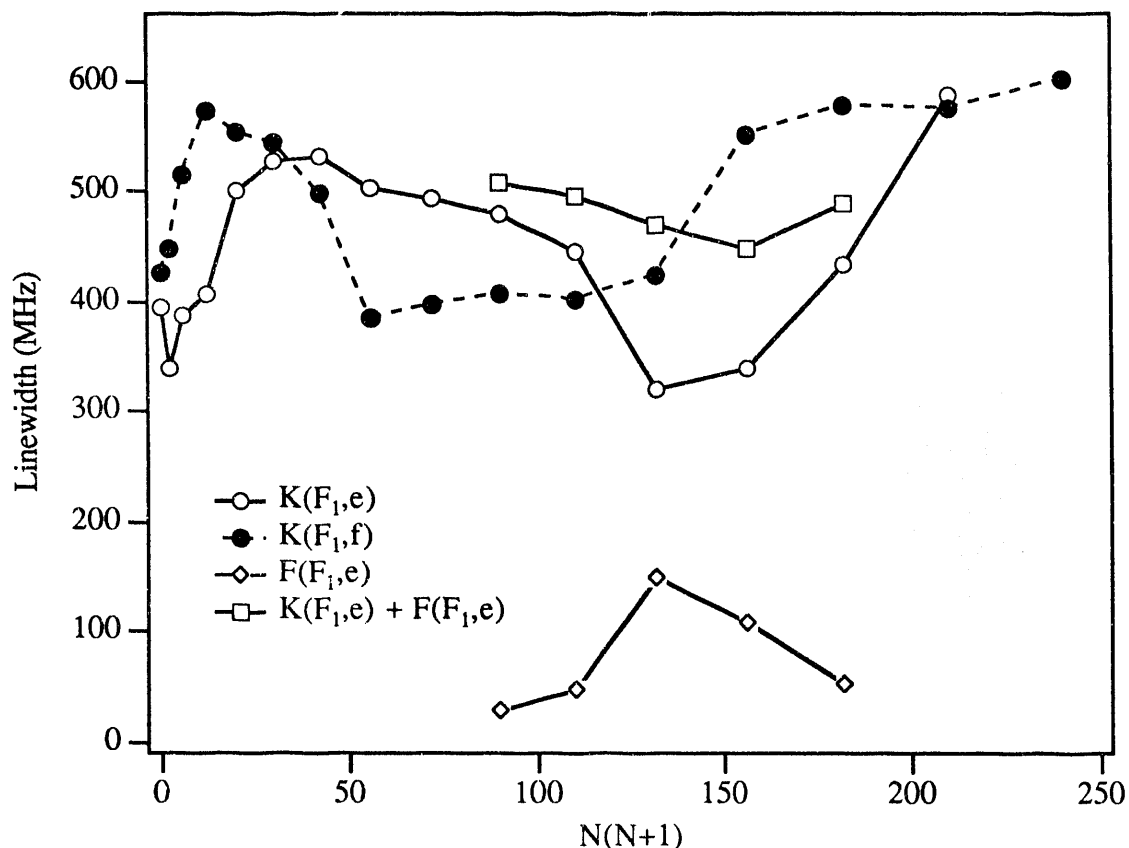


Figure 2. Natural linewidths as a function of $N(N+1)$ for selected rotational levels of the $(4p\pi)K^2\Pi(v=2)$ and $(3d\delta)F^2\Delta(v=3)$ Rydberg states of $^{14}\text{N}^{16}\text{O}$.

Initial observations of the circular dichroism of angular distributions (CDAD)³⁻⁶ in photoelectron spectra resulting from ionization of single hyperfine quantum states within the $7p^2P_{3/2}$ manifold of cesium will be presented.

CONCLUSIONS

It is anticipated that systematic, high resolution studies of small molecules, and radicals in particular, offer significant potential for development of selective and sensitive analytical methodologies applicable to atmospheric species and to diagnostic fragments generated during photodissociation of larger molecules. It is an additional premise of this research that complete

characterization of the angular momentum composition, through measurements of alignment, of such diagnostic fragments can provide enhanced analytical selectivity pertinent to determinations of chemical speciation.

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