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The principal objectives of this project were to systematically investigate the structure and dynamics of molecular Rydberg states using high resolution laser spectroscopy. We have established a new laser facility for this purpose, and have used it to accomplish several initial projects. Using laser double resonance, we have made a systematic study of Rydberg state energy level structure and autoionization in the NO molecule, particularly in the nf states. A simple theoretical model was devised, based on the long-range interaction between the molecular ion core and the excited Rydberg electron, that accurately describes both electronic structure and autoionization rates in nonpenetrating Rydberg states. We have also obtained double resonance spectra of previously unknown excited states in CO, and have been able to characterize the 3s σ state of O₂ using photoelectron spectroscopy.

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"Autoionization of the 4f Rydberg State of the NO Molecule," E.E. Eyler, W.A. Chupka, Steven D. Colson and D.T. Biernacki, Chem. Phys. Lett. 119, 177 (1985).

"Autoionization of Nonpenetrating Rydberg States of NO and H₂," E.E. Eyler, in Proceedings of the Workshop on Some Aspects of Autoionization in Atoms and Small Molecules, Argonne National Laboratory, ANL-PHY-85-3, pp. 245-252. Workshop was held May 2-3, 1985.

"Rydberg-Valence Interactions in the Π_g States of O₂," Abha Sur, C.V. Ramana, W.A. Chupka and Steven D. Colson, J. Chem. Phys. 84, 69 (1986).

"Autoionization of Nonpenetrating Rydberg States in Diatomic Molecules", E.E. Eyler, Phys. Rev. A 34, 2881 (1986).

"Rotationally resolved double resonance spectra of NO Rydberg states near the first ionization limit," D. Therese Biernacki, Steven D. Colson and E.E. Eyler, J. Chem. Phys. 88, 2099 (1988).

"Analysis of the 4f, v=3 state of NO," E.E. Eyler and D. Therese Biernacki, J. Chem. Phys. 88, 2850 (1988).

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"High resolution laser spectroscopy of NO: The A, $v=1$ state and a series of nf , $v=1$ Rydberg states", D. Therese Biernacki, Steven D. Colson and E.E. Eyler, J. Chem. Phys. 89, 2599 (1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The principal objectives of this project were to systematically investigate the structure and dynamics of molecular Rydberg states using high resolution laser spectroscopy. We have established a new laser facility for this purpose, and have used it to accomplish several initial projects:

Autoionization rates have been measured for 28 levels of the $4f$, $v=3$ state of nitric oxide. These are the first accurate determinations of decay rates in nonpenetrating molecular Rydberg states. The energy levels of these same states were measured and analyzed using a long-range interaction model to describe the perturbation of the distant Rydberg electron with the NO^+ core. The deviations from simple hydrogen atom binding energies were explained to an accuracy of 0.1% using this model.

To understand the decay rates, we have developed a theoretical model for autoionization of high ℓ Rydberg states that should be applicable to any small molecule. Decay rates for any state can be determined from knowledge of the polarizability, dipole and quadrupole moments of the molecular ion core as a function of internuclear separation. It was found that in nearly all cases where autoionization is energetically possible, it should occur more rapidly than radiative decay. Specific calculations were carried out for molecular hydrogen and compared with recent experiments.

Using optical double resonance, we have obtained completely resolved spectra of the $n=7,8$ and 9 Rydberg states of NO and conducted an extensive analysis. A previously unobserved quantum interference effect was observed and analyzed where the narrow $5f$, $v=2$ levels are coincident with the broadly predissociative $8p$, $v=1$ levels. We also obtained multiphoton ionization spectra of the $3s$ Rydberg state of O_2 , and were able to characterize this state using photoelectron spectroscopy, showing strong evidence for Rydberg-valence interactions.

A new optical double resonance arrangement using a pulse-amplified cw dye laser and a collimated molecular beam was set up to allow studies of very highly excited states with 60 MHz resolution. This apparatus was used for a systematic study of the $3s$, $7f$, $12f$ and $15f$ states of NO. The natural linewidths were fully resolved, so that both energy levels and autoionization rates could be determined by measuring the line positions and their widths. A detailed analysis of this data yielded both an improved understanding of the Rydberg state structure and a much improved value for the ionization potential of NO. Preliminary experiments were also conducted on excited states of CO, about which comparatively little is known. These preliminary runs were very successful, and clearly demonstrate the feasibility of a comprehensive study of this system using laser double resonance.

AFOSR Program Manager: Dr. Francis J. Wodarczyk



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FINAL REPORT

Laser Spectroscopy of Excited States in Atmospheric Molecules

grant number AFOSR 85-0054

1. Apparatus for double resonance spectroscopy with very high resolution

A new spectroscopic system for exciting and analyzing high Rydberg states of small molecules was developed over the course of the first two years of our grant. A pulsed supersonic nozzle is used to produce an intense beam of rotationally cold molecules. The molecular beam is collimated and crossed transversely with one or more laser beams to obtain Doppler-free spectra. Custom-designed pulsed systems that produce 1 kV pulses with negligible ringing are used to Stark ionize the molecular ion states for efficient detection. The principal laser system is a pulse-amplified cw dye laser from which we have obtained 10 nsec pulses with up to 15 mJ energies and bandwidths of about 0.002 cm^{-1} . This laser has been operated successfully from 420-800 nm; using sum-frequency mixing in the new nonlinear crystal $\beta\text{-BaB}_2\text{O}_6$, we have produced sum-frequency radiation as low as 197 nm. Our recently published spectra of Rydberg states in NO, obtained with this apparatus, exceed the resolution of previous work on high molecular Rydberg states by about an order of magnitude.

2. Pulsed discharge source for metastable molecules

We have constructed and thoroughly evaluated a supersonic pulsed discharge source for metastable atoms and molecules, an improved version of the source recently used by Johnson to investigate the Rydberg states of N_2 .¹ In the course of our research on H_2 (sponsored by NSF) we have obtained extremely intense multiphoton ionization signals both from the metastable state and from vibrationally excited levels of the ground state. Up to 10^6 ions per laser shot can be produced. We expect similar performance in other molecules, including N_2 and CO. This will greatly expand the range of excited states that we can access.

3. Structure and lifetimes of the $4f$, $v=3$ state of NO

The singly excited Rydberg states of many diatomic molecules can be regarded reasonably accurately as an NO^+ molecular ion core orbit by a distant, nearly hydrogenic

Rydberg electron. A particularly precise test of this picture can be had by studying the lowest nf Rydberg states, where deviations from hydrogenic energies are large enough to measure easily, but the structure is nevertheless simple since the nf electron does not significantly penetrate the molecular ion core. The $4f$, $v=3$ state of NO is an ideal candidate since the NO molecule is experimentally very tractable, and this particular state lies just above the threshold for autoionization into an No^+ , $v=0$ ion and a free electron. A high-resolution double resonance study of the $4f$, $v=3$ levels was obtained by using a pulsed laser to excite selected vibrational and rotational levels of the A (3σ) state, and subsequently using a single-mode cw dye laser to excite the $4f$ state. Ref. 2 discusses measurements of the autoionization rates, and Ref. 3 presents a detailed analysis of the energy levels using a long-range interaction model in which the Rydberg electron interacts with the core only via its polarizability and its static electric multipole moments.

4. Autoionization of nonpenetrating molecular Rydberg states

Since the energy levels of molecular Rydberg states with $l \geq 2$ are so well described by the long-range interaction model, it was natural to extend this simple theoretical picture to include autoionization as well. Since the quadrupole moment of the ionic core changes slightly with internuclear separation, it oscillates in size as the molecule vibrates, and this oscillatory quadrupole moment gives rise to the vibrational-electronic coupling that ionizes the Rydberg electron. Similarly, the same mechanism can lead to rotational autoionization when it is energetically possible, since the multipole tensors co-rotate with the ionic core. The resulting ionization rates can be calculated quantitatively if the core moments are known as a function of internuclear separation. Such a calculation has been carried out in detail for H_2 , where it seems to agree well with experiment. The general method and its application to H_2 are both discussed in Ref. 4.

5. Analysis of medium-resolution spectra of Rydberg states of NO and O_2

We have completed an analysis of data obtained using double resonance with tunable pulsed lasers of autoionizing Rydberg states of NO near the first ionization limit, including the $7f$, $8s$, $8p$, $8f$ and $9s$ states. Coupling to the $5f$, $v=2$ channel greatly affect the decay of the $8p$ states, and has been analyzed in detail. Where the sharp $5f$ lines are energetically coincident with diffuse $8p$ lines of the same parity, strong interaction gives rise to an asymmetric interference lineshape in the spectrum. Ref. 5 describes this work

more fully. This grant also supported preliminary work on the Rydberg states of O_2 using multiphoton ionization spectroscopy. The resulting photoelectron spectra for the $3s\sigma$ state show significant effects attributable to Rydberg-valence mixing.⁶

6. High resolution spectroscopy of high Rydberg states of NO

We have obtained spectra of several high Rydberg states of NO with a resolution of 0.002 cm^{-1} using stepwise excitation with a pulse-amplified cw laser system.⁷ A conventional pulsed dye laser is used to populate selected levels of the $A(3s\sigma)^2\Sigma^+$ state, and the high resolution system subsequently excites Rydberg states. Extensive spectra have been obtained of the $7f$, $8s$, $12f$ and $15f$ states with $v=1$. In nearly all cases the linewidths are fully resolved, allowing direct determinations of decay rates from the observed widths. Fig. 1 shows a scan over two branches to the $7f$, $v=1$ state, together with a least-squares fit to a sum of two Lorentzians. An analysis of the structure of the nf states has been carried out using the long-range interaction model, and accounts quite well for the observed energy levels. We hope that an extension of this model will allow us to understand the autoionization rates as well, using methods that can readily be generalized to other systems.

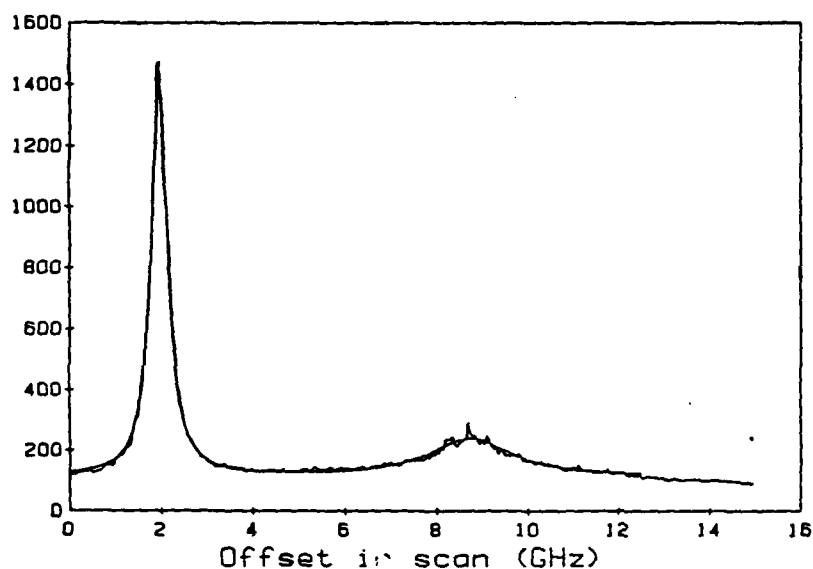


Fig. 1. High resolution spectrum of two $7f+A, (1,1)$ transitions in NO, with $N^+ = 4$, $N = 4$ and 5 . Smooth curve shows a least-squares fit to two Lorentzians.

A more interesting situation is depicted in the unpublished data shown in Fig. 2, showing the $8s, v=1$ state. This state lies just below the $v=0$ ionization limit, and is nearly degenerate with several very high $v=0$ Rydberg states. There is sufficient interaction with these states to give rise to a complex lineshape with numerous internal features corresponding to the the various $v=0$ Rydberg states. In this experiment detection was accomplished using an electric field pulse delayed by some tens of nsec to strip the Rydberg electron, indicating the state has a lifetime at least this long. Measurements of the $9s$ state, somewhat above the ionization limit, show a much more typical pattern, exhibiting a single nearly Lorentzian lineshape indicating a lifetime of nearly one nsec.

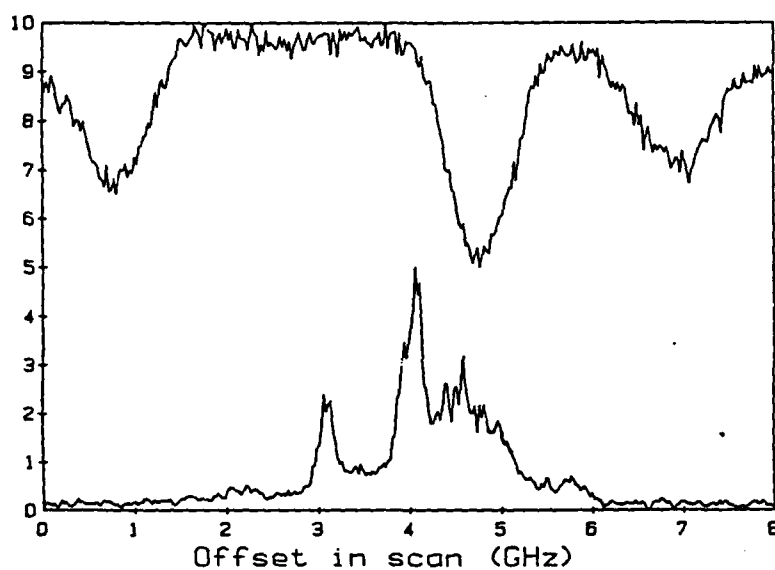


Fig. 2. Spectrum of the P(1) branch of the $8s+A, (1,1)$ band in NO, showing interference with $v=0$ high Rydberg states.

7. Precise spectroscopy of $A+X$ intervals in NO

Several $A+X$ intervals have been measured to an absolute accuracy of 0.01 cm^{-1} , to calibrate our Rydberg state studies and to serve as secondary wavelength standards in the UV. This work was performed using single-photon excitation by a blue pulse-amplified cw laser frequency doubled in a $\beta\text{-BaB}_2\text{O}_6$ crystal. Using these measurements and the

structure of the nf Rydberg states of NO, we have been able to make precise determinations of the ionization potential of NO and the electrostatic moments of NO^+ .⁷ Since the results are in disagreement with recent determinations of the IP by Muller-Dethlefs and Schlag using zero-energy photoelectron spectroscopy, this work turned out to be somewhat more interesting than we initially suspected. It led to the discovery of systematic errors in the photoelectron data caused by small stray electric fields; the corrected results are in agreement with our spectroscopic extrapolation.

8. Autoionizing $v=1$ Rydberg states of CO

As a portion of this effort we have obtained the first observations of laser excitation to vibrationally autoionizing Rydberg states of CO slightly above the first ionization limit. The only existing spectroscopy in this region is the observation of a Rydberg series in absorption spectroscopy with low resolution, somewhat arbitrarily designated as 'p' states.⁸ Recently a 3-channel MQDT analysis has been used to predict line shapes and positions for several s and p states.⁹

By using an optical double resonance technique we have made a preliminary study of autoionizing Rydberg states converging to the $v=1$ level of CO^+ , in the vicinity of $n=9$ and $n=10$. Frequency doubled light at 591 nm is used to populate the $A^1\Pi$, $v=2$ state by two-photon excitation. Rydberg states are then excited by absorption of another photon near 216 nm, generated by doubling the output of a pulsed dye laser in a newly available doubling crystal, $\beta\text{-BaB}_2\text{O}_4$. Since the spectra are obtained from selected rotational and vibrational levels of the intermediate state they are simplified greatly, especially in this region where numerous overlapping broad lines would otherwise be encountered. Figure 3 shows preliminary data in the vicinity of $n=9$, revealing several features that have yet to be identified.

These spectra can easily be extended to a range of principal quantum numbers and initial rotational levels. Experiments on N_2 can also be conducted using essentially identical techniques. Since it is isoelectronic with CO, the same methods can be used with only minor changes.

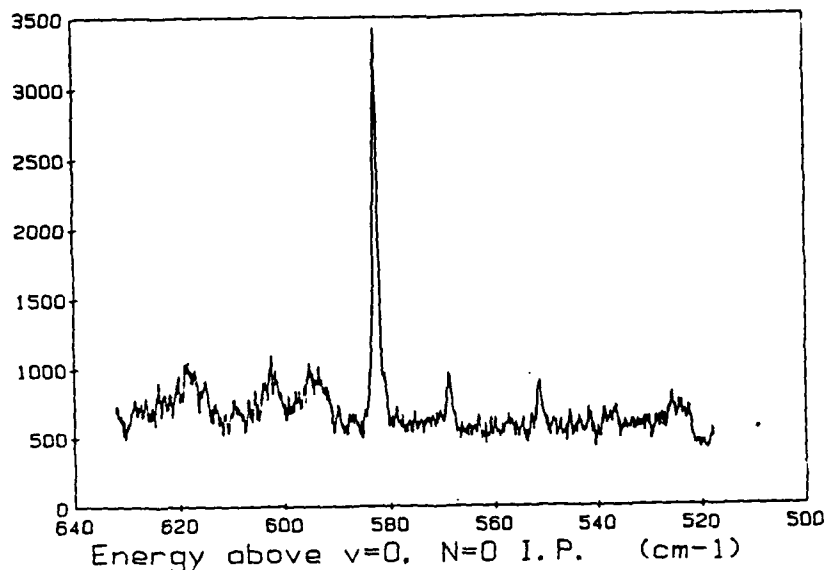


Fig. 3 Double resonance spectra of autoionizing $v=1$ states of CO in the region near $n=9$.

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