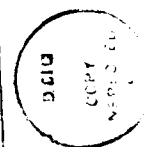


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ABSTRACT (Continue on reverse if necessary and identify by block number) Progress is described in a three-year program of research supported by AFOSR under the High-Energy-Density-Matter (HEDM) initiative. A laser-crossed molecular beam apparatus was constructed which is equipped to probe unique high-energy excited states by: (1) directly detecting anion photoproducts of charge-transfer intermediate excited states; (2) determining internal state distributions following photoionization of high-energy intermediates by time-of-flight photoelectron spectroscopy; and (3) characterizing ion-fragment distributions by time-of-flight mass spectroscopy. This instrument was employed in combination with a second, quadrupole molecular beam system to complete a set of experiments exploring structural and dynamical properties of high-energy matter. AFOSR supported experiments have detected anions arising from energetic charge-transfer configurations of monomeric HCl. Additional work on the same molecule, has probed intermediate-state effects on ion-fragment branching ratios, and, by double-resonance, characterized the dynamics of rotationally state selected spin-bit autoionization. Also developed was a means for obtaining zero-kinetic-energy photo															
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19 electron spectra of cationic rovibrational structure, which has been employed to measure precise thresholds for ionization into specific rovibrational states of HCl and NO₂. For NO₂, triple-resonant state selection has been employed to resolve a dramatic and unprecedented pattern of core-vibrational mode-selectivity in the competition between autoionization and predissociation at total energies as high as 80,000 cm⁻¹. Also begun was a promising new initiative to investigate the structure and dynamics of Group III hydrides, particularly BH_x and AlH_x, with the aim of ultimately incorporating these fragments in larger hypervalent hydride structures.

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Final Report

Title: Production and Characterization of High-Energy Hypervalent Hydrides

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Inclusive Dates: 1 September 1987
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Multiresonant Spectroscopy and Dynamics of Molecular Rydberg States, K. S. Haber, F. X. Campos, J. W. Zwanziger, R. T. Wiedmann and E. R. Grant, *Proceedings Fourth International Conference on Multiphoton Processes (ICOMP IV)*, Boulder, CO, July, 1987.

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Laser Induced Fluorescence X $^1\Sigma^+ \rightarrow A\ ^1\Pi$ Spectrum of AlH Produced by a Filament-Source Pulsed Free-Jet Expansion, Y. F. Zhu, R. Shehadeh and E. R. Grant, manuscript in preparation.

Technical Report:

Introduction

Very highly excited levels of neutral molecules and clusters present attractive opportunities for exploring important dynamics in unusual states of matter. Lying near and above first ionization thresholds, such levels occupy a regime that, though complicated by high state density, can be made accessible by application of simple contrasting limits. The Rydberg separation, for example, assembles high-lying excited states by combining a well defined molecular core, having the vibronic structure of the corresponding cation, with the diffuse charge distribution of a single promoted electron. Valence states, on the other

hand, emerge from multiple configurations of higher-energy localized molecular orbitals. Ionic or charge-transfer states constitute a third elementary separation that has attracted increasing attention, particularly in connection with new design strategies for high-energy-density materials.

Experimentally, higher-energy valence states are distinguished by their dissociative properties. Rydberg and charge-transfer states store energy more stably. The properties of high-energy systems at separable limits, as well as patterns of coupling required to form more complete descriptions, are issues of importance that can be probed spectroscopically. Excited states and their perturbations are characterized by spectral positions and intensities. For example, the spectrum of transitions to various accessible vibrational states of a given molecular ion, from a photoprepared intermediate state of the neutral, characterize that intermediate. If the intermediate is a Rydberg state near its separable limit, the well-defined ionic properties of its core insure that the photoejection of the Rydberg electron will be a highly vertical process. Charge-transfer or valence character distributes intensity more widely over those accessible vibrational (and electronic) states of the ion that span the character of the intermediate. In special cases, when the excited state has very little Rydberg character, the cross section for electron photoejection can fall to zero, with absorption leading instead to excited neutral fragments or ion pairs.

This principle of photoselection thus can serve as the basis of a highly effective spectroscopic methodology, offering a unique perspective from which to characterize the structure and dynamics of highly excited molecules and complexes. The application of this methodology in pursuit of information on high-energy dynamics is a unifying focus of our research. This research, supported under the High-Energy-Density-Matter (HEDM) initiative, made substantial progress toward fulfilling the objectives set forth in our original HEDM proposal. Our effort began with the construction of a laser-crossed molecular beam apparatus equipped to probe unique high-energy excited states by: (1) directly detecting anion photoproducts of charge-transfer intermediate excited states; (2) determining internal state distributions following photoionization of high-energy intermediates by time-of-flight photoelectron spectroscopy; and (3) characterizing ion-fragment distributions by time-of-flight mass spectroscopy. We then employed this instrument in combination with a second, quadrupole molecular beam system to complete a set of experiments exploring structural and dynamical properties of high-energy matter. Under AFOSR support, we detected anions arising from energetic charge-transfer configurations of monomeric HCl. In additional work on the same molecule, we probed intermediate-state effects on ion-fragment branching ratios, and, by double-resonance, characterized the dynamics of rotationally state selected spin-orbit autoionization. We also developed a means of obtaining zero-kinetic-energy photoelectron spectra of cationic rovibrational structure, which we employed to measure precise thresholds for ionization into specific rovibrational states of HCl and NO₂. For NO₂, we used triple-resonant state selection to resolve a dramatic and unprecedented pattern of core-vibrational mode-selectivity in the competition

between autoionization and predissociation at total energies as high as $80,000\text{ cm}^{-1}$. We also began a promising new initiative to investigate the structure and dynamics of Group III hydrides, particularly BH_x and AlH_x , with the aim of ultimately incorporating these fragments in larger hypervalent hydride structures. The following sections detail these and related findings.

Triple-resonance spectroscopy of the higher excited states of NO_2 : Mode selectivity in the competition between dissociation and autoionization

Using stepwise excitation methods, we have begun an extensive examination of specific factors that affect the dynamics of competitive channels of decay in superexcited NO_2 . This system is particularly well suited to multiresonant spectroscopic techniques, and our studies in this vein have been highly revealing.¹⁻⁵ Work just completed has established a dramatic pattern of core-vibrational mode selectivity in the high-energy radiationless decay of NO_2 via competing paths of predissociation versus vibrational autoionization. We characterize these dynamics by analyzing patterns of intensity and lineshape in ionization-detected absorption spectra of vibrationally autoionizing states, reached in transitions from selected rotational states of a number of vibrational levels within the double-resonantly prepared gateway $3p\sigma\ ^2\Sigma_g^+$ Rydberg state. Photoselection, associated with three-color triple-resonant absorption, resolves single rotational lines in discrete electronic states that lie above the adiabatic ionization threshold at total energies as high as $85,000\text{ cm}^{-1}$. Most features observed can be assigned to vibrationally-labeled $s\sigma$, $d\sigma$, and $d\pi$ series converging to associated vertical thresholds. Identified transitions typically extend over intervals of principal quantum number ranging from $n=6$ to more than 40. Observed spectra are modulated in intensity by sequences of perturbations that can be recognized as interloping series of complementary vibrational character, in which the balance of factors regulating the competition between available decay channels differs strongly.

Figure 3 below compares spectra of vertical transitions from symmetric stretch, (100), and bending, (010), excited levels of the $3p\sigma$ state. The spectrum from (100) shows a series of autoionizing resonances converging to the threshold for forming the (100) state of the cation. The intensities of these ionization-detected transitions are modulated by broad dips that form a series converging to the (110) threshold. Discrete states in these pure stretching series autoionize efficiently, as evidenced by the continuity of ionization-detected oscillator strength across the vertical threshold. The periodic mixing of bending character apparently interferes with ionization, presumably by diverting radiationless decay through neutral fragmentation channels. The behavior evidenced in the spectrum of autoionizing states reached in vertical transitions from the $3p\sigma$ (010) state confirms this hypothesis. Here we see a diminished yield from autoionization, accompanied by a definite step of increased ion yield at the vertical threshold. Thus, we can conclude that, in states with total energies near $80,000\text{ cm}^{-1}$, the presence of one quantum of excitation in

symmetric stretch is sufficient to direct radiationless decay strongly toward electron ejection, while a similarly small increment of the total energy deposited in bending excitation channels relaxation much more efficiently toward neutral fragmentation.

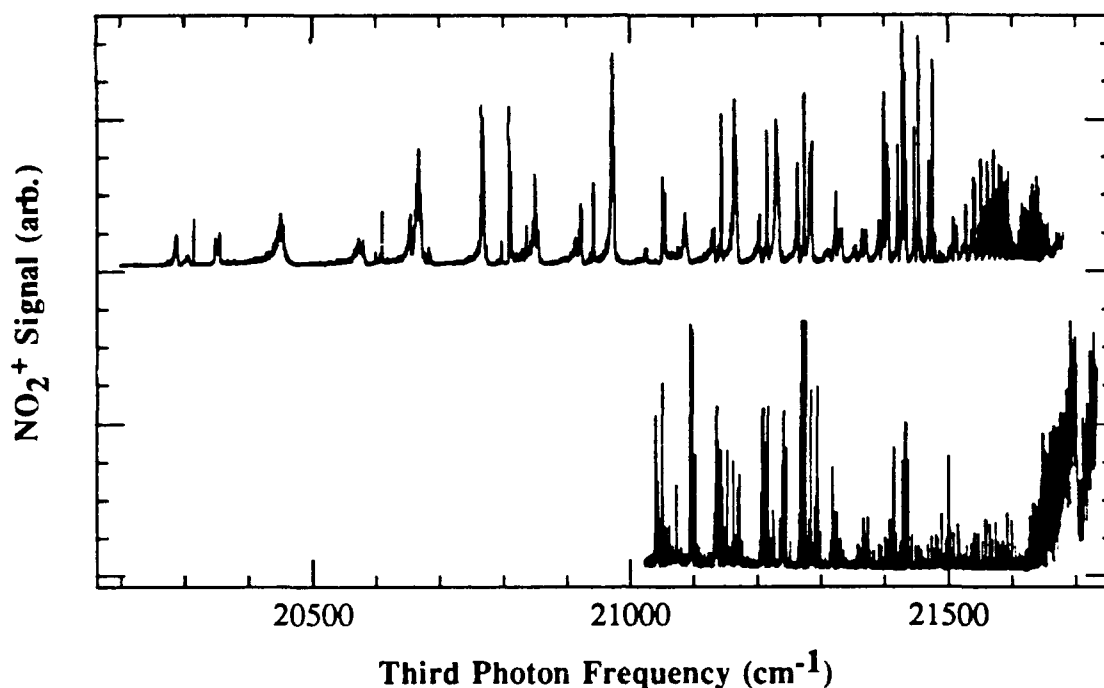


Figure 1. Ionization-detected absorption spectra of NO_2 (100) (upper) and (010) vibrationally autoionizing manifolds accessed by one-photon absorption from $N'=1$ levels of $3p\sigma^2\Sigma_g^+$ (100) and (010) states, optically selected by double-resonant excitation

Spectra in both cases span a range from the Hund's case-b limit to that of case-d coupling. Resonances generally show rotational structure consistent with the spectrum of transitions accessible and the variation expected in rotational spacing as Rydberg angular momentum systematically uncouples from the molecular axis. Autoionizing resonances differ significantly in width and lineshape, evidencing a broad variation in the strength with which discrete states are coupled with underlying continua. The data show general trends toward increasing lifetime (decreasing width) with increasing principal quantum number and increasing Rydberg electronic angular momentum, both factors conventionally taken to signify decreasing electron-core penetration. Fano lineshapes⁶ indicate components of direct, vibrationally off-diagonal photoexcitation to underlying continua, that interfere with discrete state absorption. With precise rovibrational-state selectivity afforded by triple resonance, this work offers an unprecedented opportunity to test extensions of powerful scattering-theory-based formalisms of high-energy intramolecular dynamics to polyatomic molecules.⁷

Experimental probes of coupling between elementary limits in the higher excited states of HCl

The simple diatomic hydride, HCl, has served as a prototypical molecule in our efforts to develop methods for exploring charge-transfer and proton-transfer excited states in larger molecules and complexes. We have conducted a variety of experiments preliminary to an investigation of photopreparative routes to energetic molecules of the form $MH^+ \cdot Cl^-$. Of interest are the dynamical properties of highly excited states below and above the ionization threshold. Available probes consist of ion-fragmentation patterns, photoelectron spectra, and photoanion yields. The results indicate a range of behavior.

For example, we find that the time-of-flight mass spectrum produced by two-photon resonant three-photon ionization via the $4p\pi F^1\Delta(v=0)$ state shows only the HCl^+ parent ion. Apparently, the F state, at this vibrational level, is pure Rydberg, with a well-developed core-Rydberg-electron separation from which transitions to the ionization continuum are vertical. A little higher in energy, Figure 2 shows comparative yields of HCl^+ and Cl^+ scanning over $F^1\Delta(v=1)$ and neighboring $V^1\Sigma^+(v=13)$. The V state, which has substantial valence character, apparently produces cations with sufficient internal energy to reach dissociative thresholds by subsequent fourth-photon absorption. Accessible are fragmentation routes to both Cl^+ and H^+ . Figure 3 compares a scan over this region collecting protons. Also visible in this latter scan is a smaller proton signal for

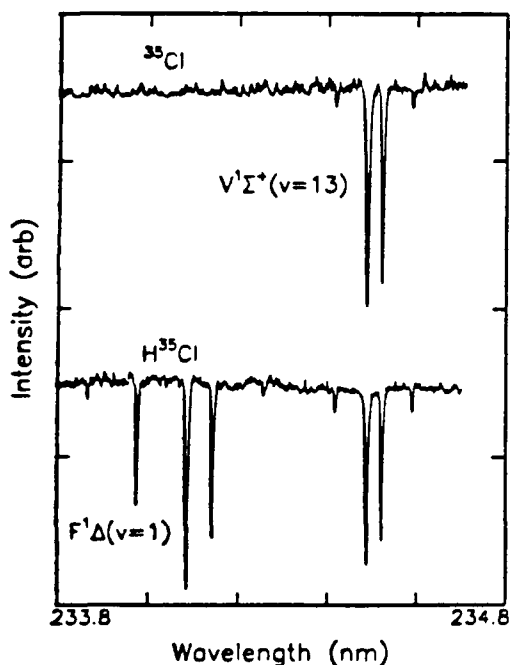


Figure 2. Comparison of Cl^+ and HCl^+ ionization-detected absorption spectra of HCl

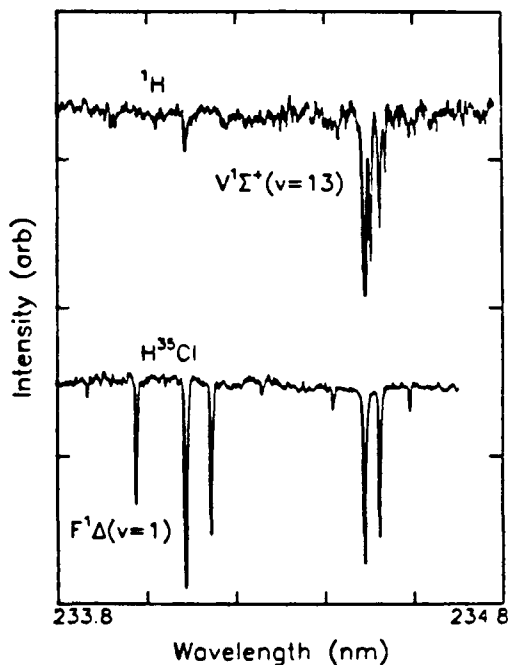


Figure 3. As in Figure 2, comparing the spectrum obtained for H^+ with that for HCl^+

the F state, which appears without an accompanying sign of the lower energy Cl^+ fragment. What we do see in this case is Cl^+ , establishing definitively that the observed H^+ signal is the cationic component of photoinduced ion-pair production. The anion spectrum additionally shows that a significant fraction of the H^+ component appearing in the V-state spectrum also arises from ion-pair production. The F ($v=0$) state yields no such ion-pair signal. One might immediately conclude from these observations that the V state and, by proximity, the F ($v=1$) state have some charge-transfer character. However, in HCl the ion-pair appearance potential lies above the ionization potential. The region of third photon absorption in these spectra includes autoionizing resonances converging to excited electronic states of the cation. We do not know the degree to which these final states mix with the ion-pair continuum in competition with that associated with electron ejection. Thus, our cation-anion mass spectra might be mapping neutral intermediate charge-transfer character, or simply sampling adventitious final-state effects. Unraveling such questions for this molecule, as well as other more complex systems may require independent control over excitation and ionization frequencies, and the routine examination of questions concerning the dynamics of ionization in competition with other fragmentation processes.

We have laid the groundwork for such investigations by extending our study of HCl to the question of its autoionization dynamics. Our initial focus has been the spin-orbit autoionizing states lying between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ ionization limits.⁸ Conventional methods fail to resolve the spectrum of this region to a meaningful level of detail because the spacing between adjacent electronic states is comparable to that between rotational states. By selecting a single rotational state ($4p\pi \text{ F } ^1\Delta v=0, J=2$) using an intermediate two-photon transition, we isolate a subset of transitions which is assignable. Figure 5 shows the experimental double-resonant spectrum of autoionizing transitions accessible from $J=2$ of the F state, together with a simulation that assumes separable Hunds case c behavior, fitting constant quantum defects and monotonically varying widths and intensities to the complete set of electronic and rotational transitions allowed by angular-momentum selection rules. Double resonance is absolutely essential to resolve this discrete structure. The indicated assignment has been made with the aid of a new capability we have developed to probe ion rovibrational structure and precisely measure thresholds by zero-kinetic-energy photoelectron spectroscopy. It can be seen that the ideal model does not correspond exactly to the data. We expect that no such simple parameterization can: Over the range of this scan, the system transforms to Hund's case e, and is subject to various levels of rotational-electronic perturbation. The simulation does, however, capture the correct density of transitions, and quite accurately describes serial structure over limited regions of the spectrum. Ultimately it is the deviations from ideal behavior that are most interesting, and the simple assignment we have made will be most useful as a starting point in identifying these. Their systematic characterization is the subject of collaborative efforts with theoreticians in the molecular spectroscopy group at Orsay.

We have now become quite routine for us to collect laser-generated anion signals, averaging the signal at the Cl^- mass, for example, while scanning the dye laser frequency to obtain rotationally resolved ion-pair detected two-photon absorption spectra. In the dimer, the potential minimum of the ion-pair state will be lowered by an amount approaching the proton affinity of HCl . It reaches its asymptotic limit, corresponding to H_2Cl^+ and Cl^- , at 8.5 eV. Under dimer-forming expansion conditions, we have searched the laser frequency region from the 293 nm two-photon threshold for ion-pair production to 240 nm. Thus far, we have found no evidence for Cl^- that we can associate with H_2Cl^+ . Apparently, despite strong thermodynamic driving forces, neutral fragmentation overrides proton transfer in the region Franck-Condon accessible from the dimer ground state.

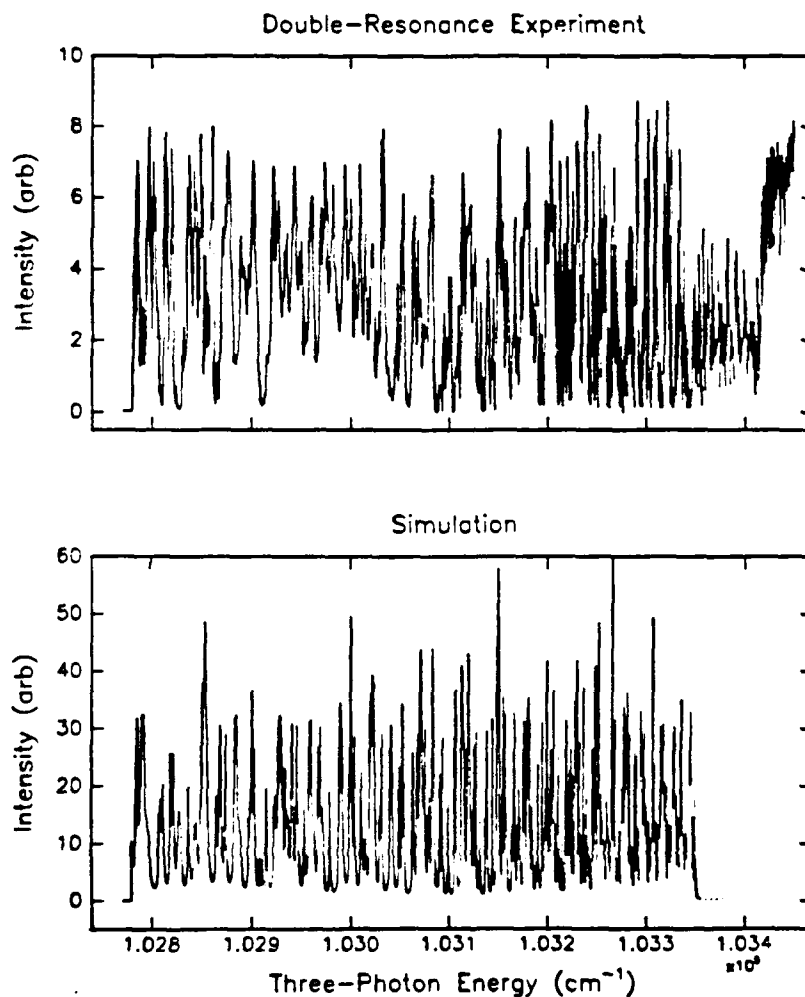


Figure 4. Ionization-detected absorption spectrum of transitions in HCl to spin-orbit autoionizing states from the $J=2$ level of the $4p\pi F^1\Delta$ state, optically selected by a preceding step of two-photon absorption. The indicated fit consists of $J=1,2$ and 3 lines belonging to noninteracting case- e Rydberg states converging to rotational levels of the $^2\Pi_{1/2}$ state of the cation.

Production and characterization of hydride fragments of boron and aluminum

Our success in developing multiresonant methods for the investigation of the dynamics of highly excited NO_2 underlies new initiatives focussed on the energetic radical fragments, BH_2 and AlH_2 . Both of these molecules are a five-electron hydrides. Walsh diagrams for five-electron systems of the type AH_2 , compare with those of seventeen-electron AB_2 molecules.⁹ Thus, a simple analogy exists between such hydrides and NO_2 ; all are extra-electron molecules, which can be expected to have a complex low-lying valence electronic spectrum, and sharp Rydberg states, evidencing a stable, electronically well-isolated, linear, closed-shell ion core. Theory, at the *ab initio* level, confirms this view of BH_2^+ , but, interestingly, predicts that AlH_2^+ is unstable with respect to Al^+ plus H_2 .¹⁰ We have made an effort to examine this question, in concert with an investigation of excited-state structure and dynamics in these and related Group III hydrides.

We have developed a variety of new pulsed molecular beam sources to form intense jets of Group III radical hydrides. Techniques tested include: (1) hot filament evaporation/pyrolysis,¹¹ (2) corona-excited supersonic expansion,¹² (3) nozzle-confined pulsed-discharge,¹³ (4) expansion-region gas-phase photolysis,¹⁴ and (5) laser ablation of solid targets.¹⁵ Our greatest success thus far has come with the filament source, which is among the most convenient to use, operating well with either a pulsed or CW inlet gas supply. The filament itself is a 1 cm x 3 mm dia. coil of 10 mil tungsten or tantalum wire. It is held in a 1 x 0.25 in. dia. alumina tube, which serves as an outlet for a Newport pulsed molecular beam valve. Powered by a few Watts, the filament easily pyrolyses a mixture of diborane in H_2 to yield boron hydride fragments. To form aluminum hydrides, we wrap tungsten wire with aluminum wire, and wind the resulting coil into a filament. Upon heating, the aluminum wets the tungsten and evaporates. A pulsed jet of hydrogen carrier passing through the hot zone reacts with atomic aluminum to form molecular hydrides. Figure 5 shows a spectrum of AlH produced using this source.

Efforts are presently underway to optimize conditions for the formation of higher hydrides. Immediate plans call for multiple-resonance experiments to probe higher excited states. We shall be interested in characterizing Rydberg and autoionizing states of BH and AlH . We will then take up the question of ion-core structure and stability in BH_2 and AlH_2 . We will extend characterization of our molecular beam sources to look for larger molecules and clusters. Of particular interest will be efforts to photoproduce hypervalent cores within boron- and aluminum-centered hydrogen clusters. These, we believe, will best be generated in a liquid-nitrogen cooled nozzle following mild laser ablation of elemental boron or aluminum in a high-pressure H_2 expansion. Finally, all the fragment and cluster, pulsed and CW nozzle technologies we develop for isolated-molecule spectroscopy will find wide application in condensed-phase experiments planned for the near future.

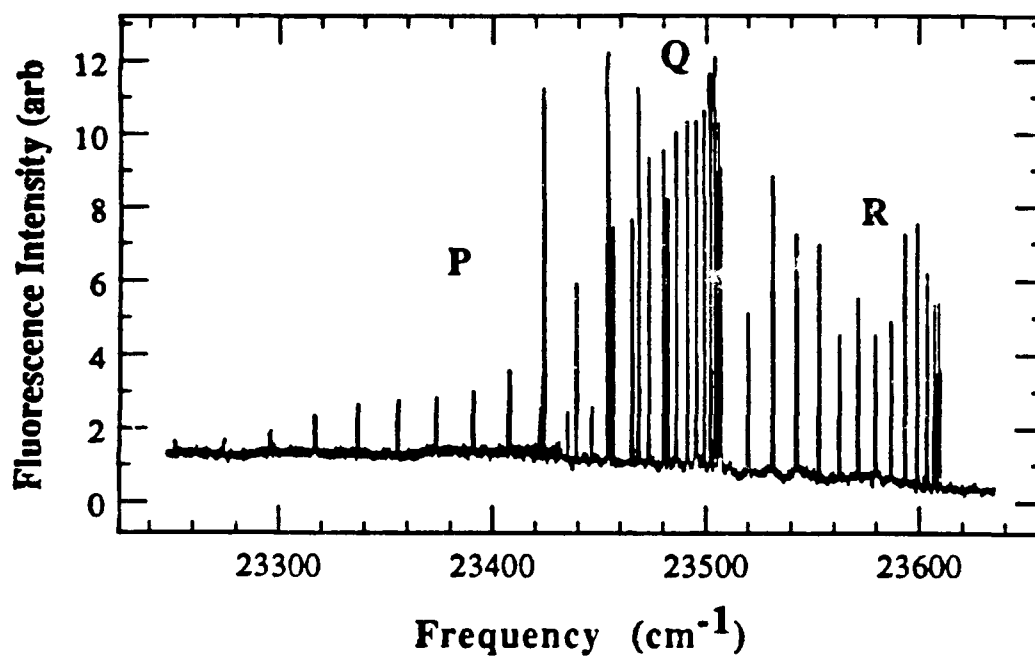


Figure 5. Laser-induced fluorescence spectrum of the (0,0) band of the $^1\Sigma^+ \rightarrow ^1\Pi$ transition in AlH produced by filament-source pulsed supersonic expansion.

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