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RESEARCH AT LOS ALAMOS

AUTHOR(S): C. PAUL ROBINSON AND REED J. JENSEN

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scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

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SOME DEVELOPMENTS IN LASER ISOTOPE SEPARATION^{*}
RESEARCH AT LOS ALAMOS

BY

C. Paul Robinson and Reed J. Jensen
Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico 87545

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I. Introduction

This work began at LASL in 1971 as part of a comprehensive program on laser separation of uranium isotopes. We made the early decision to concentrate efforts on molecular systems because of the higher volatility and modest total laser energy needed to produce a stable chemical change that would facilitate physical separation of photolysis product. As the field has developed and important parts of the concept have appeared in the literature, this area of our work has been declassified and we are able to report some theoretical and experimental results.

Today we would like to discuss the supersonic expansion of bulk gas samples to obtain low vibrational and rotational temperatures that allow detailed resolution of the infrared absorption features of isotopic molecules; in this case $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$. This principle was first discussed in the literature by Sinha, Schultz and Zare,¹ and later by Smalley et al.², and D. I. Kataev and A. A. Mal'tsev.³ This information was just released prior to this meeting. We anticipate a large number of scientific papers to be published during the next year, describing various aspects of the physics involved. There have been a number of fundamental advances made and there have been a large number of our co-workers at Los Alamos who have participated in the work. The next slide lists some SLIDE of the principal scientists involved on the research team.

II. Basic Concept

In the molecular approach to LIS, one of the processes we have investigated is the two-step dissociation of molecules, by first selectively exciting a bound state through an isotopically shifted optical transition and then dissociating the excited state. The molecular form is to be selected such that the photolysis product is easily separable from the initial compound. The basic premise is that the excited state will have a much larger photodissociation cross-section than unexcited molecules. This preliminary selective excitation can also be of the multistep type discovered by Lyman et al.⁴ and independently by Ambartzumian et al.⁵. In this case at sufficient intensities, no ultraviolet or visible radiation is required in order to achieve dissociation.

SLIDE 1
& SLIDE 1A

This simple picture of state selective photochemistry is complicated in practical systems by the fact that at temperatures where the working molecules have interesting vapor pressures most polyatomic molecules are not all in the ground state, but are distributed over the various energy states. As is well known, uranium containing molecules with any appreciable vapor pressure exist only as polyatomics. For example, the distribution of UF_6 molecules at room temperature is shown in slide 2. UF_6 has the highest vapor pressure of any uranium molecule by about two orders of magnitude. Slide 3 shows the Boltzmann equations used to obtain the distribution and slide 4 shows the fractional population of the ten lowest lying states as a function of temperature.⁶

SLIDE 2

SLIDE 3

SLIDE 4

The excited states have anharmonicities associated with specific vibrational transitions so that each state has its own spectrum. The observed infrared absorption in room temperature UF_6 are composite spectra of the various energy states weighted by their equilibrium populations. This is depicted in slide 12A below.

An obvious way to collapse all the population into the ground state is by cooling. However, at the temperature required to collapse over 90% of the molecules into the ground state, UF_6 has essentially no vapor pressure. Non-equilibrium cooling, if accomplished in a sufficiently rapid manner as to prevent condensation of the supersaturated gases, can overcome the vapor pressure difficulties. Over the past three years, we have applied this technique to a number of polyatomic gases. The methods applied present a generally useful technique for the basic study of polyatomic molecules. Theoretical understanding is greatly facilitated through the fundamental information which can be measured under the unique conditions which can be experimentally achieved.

III. Gas Dynamic Expansion

If UF_6 or other low γ gas is mixed with a high γ gas (helium, argon, nitrogen, etc.) and expanded in a supersonic nozzle, a significant supersaturation and cooling will occur and under appropriate conditions a high density of ground state molecules can be obtained. This has been successfully achieved for SF_6 and UF_6 . One method for carrying out such an expansion is shown on slide 5. The diagram represents a two-dimensional nozzle, having a slit throat, much like the first gas dynamic lasers. Notice that the expansion occurs very rapidly within a short distance of the throat, in this region called the kernel. High Mach numbers can be achieved in a uniform flow region of a central core, bounded on each side by thin boundary layers. Note that in such a geometry the gas retains all fluid properties due to the high collision rate of the collision dominated regime. Although the gas retains its full kinetic temperature of the upstream region, the static temperature is given approximately by:

SLIDE

$$\frac{T}{T_0} = \left(\frac{P}{P_0} \right)^{\frac{\gamma-1}{\gamma}}$$

so that for modest pressure ratios, the cooling is substantial. When a polyatomic gas mixture is expanded, one must compute the downstream temperature using a variable γ formulation including boundary layer growth. Using a full kinetics code for the hydrodynamics of the expanding gas, we had predicted that full equilibration could be achieved among the molecules so that translation, vibration, and rotation remain strongly coupled throughout the expansion. The only process remaining out of equilibrium is polymerization. Supersaturation ratios in excess of $\Delta T = 100$ K are easily achievable. The bulk fluid moving by at high velocities makes a unique optical medium for spectroscopic study. As you will see, great spectral simplifications result, even for the most complex polyatomic species.

The next slide shows the spectrum of the ν_3 band of SF_6 at 300 K SLIDE 6
measured with a very good conventional instrument. We (along with Brunet) had postulated that the structures shown here are due to hot bands. Indeed, the experimental spectrum could be exactly predicted by assuming that individual transitions $(\nu_1, \nu_2, \nu_3, \dots, \nu_6) \rightarrow (\nu_1, \nu_2, \nu_3 + 1, \dots, \nu_6)$ had a simple P, Q, and R structure, assigning a statistical weight to each vibrational state according to the fractional population predicted by the Boltzmann distribution of hot bands. Notice the assignments which are made, all with negative anharmonicities.

One predicts, therefore that if such a model is valid, and if the predictions of conditions for supersonically expanded gases are valid, all of the hot bands should disappear, putting the integrated absorption intensity into a single P, Q, R structure. Actually the data shown here were taken on a supersonic flow device (at Los Alamos), however after flow had been terminated. A few seconds earlier, during the supersonic flow, the same instrumentation recorded the spectrum shown on the next slide. Notice SLIDE 7
the very simple P, Q, R structures. The Q branch is slit resolution limited. Notice, however, the already large increase in absorbance. Our flow instrumentation predicted a temperature of 55 K and by measuring the distance between the maxima in the P and R branches, a temperature of $\sim 55 \pm 5$ K was deduced from the spectroscopic data. In order to reduce the error of the spectroscopic determination, higher resolution data is required.

This was the next part of our study. With laser diode capability supplied by Lincoln Laboratory (under a contractual relationship which began in 1973), we married these high resolution devices to the unique molecular conditions of the supersonic flows The next slide shows some SLIDE 8

earlier data of Hinkley et al., on SF_6 at room temperature. Note the extreme complexity of the spectra obtained at the conditions of 10^{-3} cm^{-1} Doppler width and laser resolutions of 10^{-6} cm^{-1} . Please observe the complicated structures due to both hot-band vibrational states, rotational states, and other effects. I shall return to this data later in the talk and show you state assignments we have been able to make for this data.

We published some of these values during the summer of 1974 in which we presented the data shown in the next slide, which was measured at 130 K SLIDE in a statically cooled cell. This slide shows a scan of cooled (here statically) SF_6 using such a diode laser. Note that there are completely resolved P and R lines, some real structure on the Q branch, and splitting of the higher J lines. The data shown here is the ν_3 vibrational mode. These data, along with similar data for the ν_4 mode enabled us to obtain values of spectroscopic parameters which are greatly enhanced in accuracy over any previously obtained. Very accurate force-field determinations were made using these data. About 90% of the molecules are in the ground state at this temperature. The contrasts are very striking between these data and either the room temperature data (with both conventional or diode resolution) or the flow-cooled data with conventional resolution. We can unambiguously assign rotational quantum numbers to all the transitions. However, the richness does not stop here. Notice the splitting of the high J lines. The next slide shows a scan of this splitting at even SLIDE 1 higher resolution. A group of theorists at Los Alamos, who had access to this data (and U_6 data also) since early in 1974 have developed a new formulation of group theory as applied to molecular structure. This important work has been accepted for publication in Reviews of

Modern Physics. Note here the symmetry components which are unambiguously made and assigned to each of the rotational lines. These splittings are due to Coriolis effects which are rigorously included in their theoretical Hamiltonian.

Such success in spectrally simplified data of cold gases inspired our theorists to make predictions for the very complex room temperature data. The next slide shows a typical match of theoretical assignments for Hinkley's earlier data. Once again the full quantum number assignments are unambiguous. Shown here is only a small region of data which they have analyzed. This work is being submitted for publication. SLIDE 11

Of course, a crucial question is the applicability of these same techniques for other polyatomics, especially those for which spectral simplification does not occur for temperatures which can be achieved under ordinary circumstances. I am happy to tell you that data of this type was first obtained for UF_6 , and that the analyses of our theorists were motivated by this unique data.

The next slide compares room temperature data of the ν_3 mode of UF_6 with flow cooled data taken in our supersonic flow apparatus with a conventional spectrometer. The optical absorption here vanishes and the strong Q branch appears, again slit resolution limited. The P and R branch lines are not visible here because their extremely narrow width at the 55 K temperature here is negligibly small when compared to the line spacing and the slit width. The resultant absorptions of these lines is too small to be detected with the conventional spectrometer. Again the very high resolution of a tunable laser diode is required. SLIDE 12

The next slide shows a portion of a high resolution scan of flow cooled UF_6 using a laser diode fabricated by Ken Nill, who was then SLIDE 13

at Lincoln Laboratory. Notice again these are individual R branch lines whose rotational quantum numbers can be unambiguously assigned. Note again the splitting of the lines due to Coriolis with our theoretical assignments of the split symmetries.

I am sure the question has already arisen in your minds as to the possible isotope effects that might arise from the spectral simplifications that result from the simultaneous application of dynamic cooling techniques and high resolution lasers. Isotope effects are pivotal in using such technologies in laser isotope separation processes.

The final slide shows a diode laser scan of the $^{235}\text{UF}_6$ ν_3 mode Q branch relative to some individual rotational lines of $^{238}\text{UF}_6$. The flow temperature is approximately 30 K. The additional lines shown (numbers 1, 6, and 7) are calibration lines of reference gases. One can see that the isotope selectivity here is essentially complete. SLIDE 14

Thus in conclusion, much physical understanding of the structure of molecules, and their spectroscopic properties can be deduced from the application of continuum expansion cooling, especially when used in conjunction with high resolution tunable lasers. Again I would like to acknowledge the many contributions of the members of our large research team and to thank the Atomic Energy Commission and the Energy Research & Development Administration for the support of our work.

Thank you for your attention.

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MAJOR PARTICIPANTS

PATENT AUTHORS: C. PAUL ROBINSON

REED J. JENSEN

THEODORE P. COTTER

KEITH BOYER

NORMAN R. GREINER

J. AL SULLIVAN

JACK P. ALDRIDGE

D. F. SMITH (ORGDP)

W. BURTON LEWIS

Dissociation
Limit

Two Photon
Dissociation

Multiple Photon
Dissociation

{

 Simultaneous

 Infrared

 +

 Ultraviolet

{

 Infrared

 at High

 Peak Intensity

2

Vibrational Energy Distribution in UF_6

3

Population Distribution

The contribution, dO_{vib} , to the vibrational partition function, O_{vib} , from a particular level i is given by

$$dO_{vib}(i) = D(i) \exp \left[(-h/kT) \{ \nu_1 v_1(i) + \nu_2 v_2(i) + \nu_3 v_3(i) + \nu_4 v_4(i) + \nu_5 v_5(i) + \nu_6 v_6(i) \} \right]$$

where

$$D(i) = [v_2(i) + 1][v_3(i) + 1][v_3(i) + 2][v_4(i) + 1][v_4(i) + 2][v_5(i) + 1][v_5(i) + 2][v_6(i) + 2] \div 16$$

and

$$\nu_1 = 667.1 \text{ cm}^{-1}$$

$$\nu_4 = 186.2 \text{ cm}^{-1}$$

$$\nu_2 = 532.5 \text{ cm}^{-1}$$

$$\nu_5 = 202.0 \text{ cm}^{-1}$$

$$\nu_3 = 624.0 \text{ cm}^{-1}$$

$$\nu_6 = 142.0 \text{ cm}^{-1}$$

Since the rotational width at half maximum is about 20–50 cm^{-1} , the contributions to O_{vib} have been summed over each 50 cm^{-1} interval in energy.

4

Population of low-energy vibrational states of UF₆

$$G(E,T) = \int_0^E g(y) e^{-y/KT} dy$$

TWO DIMENSIONAL EXPANSION NOZZLE

61

SF₆ at 300° K

$\Delta\nu \sim 0.1(\text{cm}^{-1})$

FIGURE 8

Diode Laser Scan

SF₆ Pressure: 0.1 Torr

Cell Length: 10 cm

Resolution: $3 \times 10^{-3} \text{ cm}^{-1}$

E.D. HINKLEY

APPLIED PHYSICS LETTERS

16, 351 (1971)

Grating Spectrometer Scan

SF₆ Pressure: 0.1 Torr

Cell Length: 25 cm

Brunel and Perez, 1969

C52-421A

INFRARED SPECTRUM OF P₁₃ BAND OF SF₆

FIGURE 7

9✓

10 v

947.0 cm^{-1}

HIGH RESOLUTION LASER SPECTROSCOPY

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UF₆ ABSORPTION: ν_3 at 300 K

13

UF₆ ABSORPTION: ν_3 at 300 K

UF_6 Infrared Absorption

Increasing Frequency →