CONF-8209193--3

DE84 001942

LECTURE 2

ONE-ATOM DETECTION AND STATISTICAL STUDIES WITH RESONANCE
IONIZATION SPECTROSCOPY*

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September 1982

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* Research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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1. Introduction

To learn how to take matter apart atom-by-atom and to count each atom according to its type, regardless of its initial chemical or physical state, is presumably a worthy goal in scientific research.¹ The advent of the laser created real hope that these aspirations will be realized. The counting of atoms is not merely an intellectual exercise set apart from real-world applications. On the contrary, even though the capability is scarcely more than five years old, practical applications have been made in many fields of chemistry, physics, the environment, and industry. In this lecture we wish to review how the laser made possible the counting of atoms and how this capability has been put to use in situations where atoms are free to react chemically as they diffuse through a medium. Fluctuation phenomena and statistical mechanics can also be examined in these situations.

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2. Cne-Atom Detection

Both the high selectivity and the extraordinary sensitivity of resonance ionization spectroscopy (RIS)¹ were demonstrated by pulsing a laser directly through a proportional counter (see Fig. 1). It was shown by Curran et al.² in 1949 that the improved version of the 1908 Rutherford-Geiger electrical counter (now known as a proportional counter) can be used to count single electrons at thermal energy. Therefore, when lasers are used to remove one electron from all of the atoms of a selected type, one-atom detection is made possible. Proportional counters are normally filled with gases like Ar (90%) and CH₄ (10%). But, for example, a pulsed laser tuned to 4555 Å can ionize with unit efficiency each atom of cesium without producing background ionization of the counting gas. In the original demonstration³ of one-atom detection at the Oak Ridge National Laboratory (ORNL) it was proven that one atom of cesium could be selected out of 10^{19} atoms of the counting gas (Ar and CH₄).

Another important form of atom counting involves the time-resolved detection of a single daughter atom in flight following the decay of a parent atom. Thus, it was shown⁴ that an individual atom of cesium could be counted from the fission decay of an individual atom of the isotope ²⁵²Cf. The energy released in the fission process generated a signal in a charged particle detector that triggered the laser used to accomplish the RIS process $\text{Cs}(\omega_1, \omega_1 e^-) \text{Cs}^+$. The experiment proved that daughter atoms can be counted in coincidence with the decay of parent atoms. Such techniques could eventually work for most of the daughter atoms associated with radioactive decay and

could possibly be used to reduce backgrounds greatly in low-level counting facilities.

2. Classical Chemical Physics Applications

The capability for detecting a population of just a few atoms has made it possible to investigate some problems in classical chemical physics which previously were difficult or impossible. Precision measurements of the diffusion of free atoms amongst other atoms and molecules have been made in sufficient detail to test the basic diffusion equation in both time and space domains. The determination of rates of reactions of extremely reactive species (such as alkali atoms) with other atoms or molecules is now possible. Since only a few of these reactive atoms need to be produced, several problems concerning corrosion of the apparatus and the production of complicated chemical by-products are avoided. Study of a population of a few atoms (e.g., 10) to observe their statistical behavior has been made.

These measurements of the diffusion, chemical reaction, and statistical fluctuation of atoms are best made by starting with a chemically inert source such as an alkali-halide molecule. Upon photodissociation of CsI (for example) with a pulsed laser in the ultraviolet (UV) region, a well-defined source of cesium atoms is produced along the narrow laser beam at some time, say $t = 0$. At any time $t > 0$ another laser can be pulsed to detect cesium atoms if they exist as free atoms in the path of this detector laser.

For a line geometry the appropriate diffusion equation is

$$\frac{\partial n(\rho, t)}{\partial t} = D \nabla^2 n(\rho, t) - \beta n(\rho, t) ,$$

where ρ is the distance between source and detector, t is the time, D is the diffusion coefficient, and β is the rate constant for loss due to chemical reactions. The solution for the concentration of free atoms $n(\rho, t)$ is

$$n(\rho, t) = \frac{\lambda}{4\pi D t} \exp(-\rho^2/4Dt) \exp(-\beta t) .$$

for a line source of λ atoms per unit length created at $t = 0$ and located in an infinite medium. The source and detector can be assumed to be well separated from any surfaces since atoms are both liberated and detected with pulsed laser beams. The data can be analyzed to obtain β and D . We note that the quantity $n(\rho_1, t)/n(\rho_2, t)$ is independent of β but contains D ; thus, precision measurement of D can be made, even when the chemically reactive medium has a large β . Experiments are done at two different separations between the source and detector lasers so that chemical effects can be cancelled in the ratio $n(\rho_1, t)/n(\rho_2, t)$. These methods have been used to obtain the diffusion coefficient for cesium atoms and for lithium atoms in several gases or gas mixtures. Besides providing more accurate measurements of the diffusion coefficients for these difficult chemical environments, the method has possible fundamental value. Since both time and space resolution are inherent in the method, it

provides a very detailed test of the validity of the diffusion equation itself.⁵

Studies have also been made to obtain the reaction constant β in various chemical environments. Thus, Grossman et al.⁶ studied the reaction of cesium with O_2 in various atmospheres of both helium and argon. Similar experiments have been reported by Kramer et al.⁷ for lithium atom reactions with O_2 in helium and argon. These were slightly more complex laser experiments since one laser at 2950 Å was used to detect lithium in the RIS scheme $Li(\omega_1, \omega_2, e^-)Li^+$ with ω_1 corresponding to 6708 Å and ω_2 corresponding to 6104 Å. The source laser and the detector lasers all overlapped in space, this being the geometry in which chemical effects are most easily separated from diffusion losses. Complex pressure-dependent data suggest that the reaction of lithium with O_2 to make stable LiO_2 proceeds both by energy transfer from intermediates like $(LiO_2)^*$ and O_2 reactions with intermediates like $LiAr$.

A particularly interesting experiment in statistical mechanics has just been completed in our laboratory.⁸ Einstein⁹ discussed a gedanken experiment to test the ergodic hypothesis for the case of freely diffusing atoms. Essentially, the experimental geometry is the one considered by Einstein except he visualized an infinite plane source and an infinite plane detector instead of a line source and a line detector. In any case, two tests of the solution to the diffusion equation could be visualized. In one case a large number of atoms would be released at $t = 0$ and the detector would essentially measure the density function $n(\rho, t)$ on each trial for a particular ρ and t . This method was called a space summation method. Einstein's

time summation method was visualized as a process where a small number of atoms would be released at $t = 0$, such that the detector at ρ and t would surely count the rare gas atom arriving at the detector. A series of trials are required so that probabilities are involved in estimating $n(\rho, t)$. If the space summation method and the time summation method agree, the system is ergodic. Our results of an actual experiment are shown in Fig. 3. In basic terms, the gedanken experiment visualized by Einstein could actually be done in the laboratory because we can now count individual atoms. Furthermore, the experiment was actually convenient because of a special property of the proportional counter - namely, it is a good digital device for counting one electron (thus one atom, assuming saturated RIS) and a good analog device for summing many electrons (thus many atoms) created by one laser pulse.

4. Analytical Chemistry Applications

The use of RIS in analytical chemistry has been reviewed by Young et al.¹⁰ and by Hurst.¹¹ The essential advantages of RIS to any analytical system are selectivity, sensitivity, and generality to nearly all of the elements.

An example of an analytical application of RIS that requires only lasers for selective ionization and proportional counters for sensitive detection is the development by Mayo et al.¹² at the National Bureau of Standards (NBS). They have developed Laser Ablation and Resonance Ionization Spectroscopy (LARIS) for the analysis of a few impurity atoms in a solid sample. With LARIS a layer is used to ablate atoms from a solid, followed with a laser for

RIS of the neutral atoms. Using a proportional counter as an electron detector, the NBS group was able to detect down to 5×10^{11} sodium atoms/cm³ of electronics grade silicon, or one atom of sodium in 10^{11} atoms of silicon. Since one electronic device in modern VLSI technology has only 5×10^{10} atoms of silicon, the NBS sensitivity for sodium was such that less than one atom of sodium per device could be detected.

The combination of a RIS ionization source and a mass spectrometer provides the best features of two methods. Essentially, a RIS source for a mass spectrometer provides selectivity on Z and the mass analyzer provides selectivity on A. With both Z and A selectivity, many interferences associated with electron ionization can be eliminated and isobars can be distinguished. The use of the laser as an ionization source for a mass spectrometer is a very natural idea and received attention in a 1976 paper by Letokhov,¹³ who suggested the combination of lasers and mass spectrometers for more definitive molecular spectroscopy.

A particular interesting example of the combination of RIS with mass spectrometers has been proposed^{14,15} for isotopically selective counting of noble gas atoms. Essentially, Maxwell's sorting demon can be made to work with the intelligence to recognize even an isotope of an atom and with the memory capacity to store and count each atom (see lecture 3 by Payne and Hurst).

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Fig. 1

Fig. 2

Fig. 3

Figure Captions

Fig. 1. Schematic of an experiment conducted to prove that RIS can be used to detect a single atom.

Fig. 2. An example of diffusion data using the RIS detection method and showing the diffusion of cesium atoms from a line source to a line detector.

Fig. 3. Experimental data obtained on Einstein's "gedanken" experiment to illustrate the ergodic hypothesis.