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RESEARCH DIRECTED AT DEVELOPING A CLASSICAL THEORY
TO DESCRIBE ISOTOPE SEPARATION OF POLYATOMIC MOLECULES
ILLUMINATED BY INTENSE INFRARED RADIATION

Final Report
for Period May 7, 1979 to September 30, 1979
Extension December 31, 1979

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ABSTRACT

This final report describes research on the theory of isotope separation produced by the illumination of polyatomic molecules by intense infrared laser radiation. This process is investigated by treating the molecule, sulfur hexafluoride, as a system of seven classical particles that obey the Newtonian equations of motion. A minicomputer is used to integrate these differential equations. The particles are acted on by interatomic forces, and by the time-dependent electric field of the laser. We have a very satisfactory expression for the interaction of the laser and the molecule which is compatible with infrared absorption and spectroscopic data. The interatomic potential is capable of improvement, and progress on this problem is still being made. We have made several computer runs of the dynamical behavior of the molecule using a reasonably good model for the interatomic force law. For the laser parameters chosen, we find that typically the molecule passes quickly through the resonance region into the quasi-continuum and even well into the real continuum before dissociation actually occurs. When viewed on a display terminal, the motions are exceedingly complex. As an aid to the visualization of the process, we have made a number of 16 mm movies depicting a three-dimensional representation of the motion of the seven particles. These show even more clearly the enormous complexity of the motions, and make clear the desirability of finding ways of characterizing the motion in simple ways without giving all of the numerical detail. One of the ways to do this is to introduce statistical parameters such as a temperature associated with the distribution of kinetic energies of the single particle. We have made such

an analysis of our data runs, and have found favorable indications that such methods will prove useful in keeping track of the dynamical histories.

This final report describes research on the theory of isotope separation produced by illumination of polyatomic molecules by intense infrared laser radiation. Such processes are investigated by integrating Newton's classical equations of motion for the atoms of the SFB6S molecule taking into account the effect of interatomic forces and the interaction of the particles with the laser field. The support under contract EN-77-S-02-4294 A001 was for the period May 7, 1979 to September 30, 1979 with a no-cost extension through December 31, 1979.

Reference may be made to the application proposal leading to this contract, dated July 11, 1978, for background information. The general plan for the research was as follows: A series of computer programs was developed for the purpose of integrating the Newtonian equations of motion of the seven atoms. The goal was to find a suitable interatomic potential and a realistic form for the laser-molecule interaction. The data base required for representation of the long-term dynamical motion of a system of seven particles could easily run to over a million computer words. Therefore, it was important to find ways to deal with the expected large amount of computer output so as to be able to develop intuition and gain understanding of the complex physical processes involved in multiphoton molecular excitation.

At the start of the research period, we had a satisfactory expression for the interaction of the lasers and the molecule. The interatomic potential mainly involved a number of two-body forces. These were based on inverse powers of the distances, making a generalization of a Lennard-Jones 6-12 potential. As explained in the proposal, it was also necessary to have

some non-central forces, and these were included by introduction of three-body Axilrod-Teller potentials. The various terms in the potential energy were given numerical coefficient multipliers. These had to be chosen so as to properly describe a number of important molecular properties. Among these were equilibrium configuration, the six distinct frequencies of the 15 normal modes of vibration, and the dissociation energy of the molecule. A systematic procedure is available for determining the numerical coefficients. Although ideally this method should succeed, in practice a number of unpleasant surprises could, and did, occur. The above-mentioned experimental quantities can be fitted with relative ease. They mostly involve the properties of the molecule near its equilibrium configurations. It easily turns out that when these are fitted, the potential can behave badly in other regions of the molecular configuration space. In particular, the potential may have lower values at some other configuration than the experimental equilibrium one. Also, the forces may misbehave in various ways at long and at short distances. Despite this, we were able to find a potential that gave reasonably good eigenfrequencies for the two optically active normal modes. The important resonance phenomena in the early stages of the LIS process should be fairly well described under these circumstances. On the other hand, the nonlinear interactions between all normal modes are vital for escape into the "quasi-continuum" and ultimate dissociation. So we continued to strive for a better potential. It was clear that our general method would work much better if we tried to make up the two-body potential functions out of more suitable building blocks than inverse power law terms. Also, the Axilrod-Teller potentials are expected to be valid

only asymptotically for large particle separations and they become singular for small distances. We needed to bring in some potential types more in accord with chemical intuition, and we had to pay more attention to getting an adequate description of the various molecular fragments SFB5S, SFB4S,... In particular, ionic forces play a very strong role in the behavior of SFB6S.

We have now incorporated a number of new potential types into our computer programming. These include an ionic potential that realistically describes the effect of charges on the S and F atoms. This depends on the relative positions of all seven particles. We also have a number of exponential function two and three-body potentials that can more realistically describe interparticle repulsive forces.

The method for determining the constants in the potential function originally worked only for constants that entered linearly as multiplying factors to the various terms. Such things as exponential decay constants, or the parameters in a Morse potential, enter nonlinearly. In principle, such constants could be determined by a nonlinear regression scheme, in which some suitable measure of the discrepancy would be minimized. This measure could be a sum of squares of differences between experimental and calculated quantities. Such a procedure would be very time consuming, and likely lead to a large number of local minima in the multidimensional configuration space. (Imagine trying to find the lowest point in the state of Arizona. It would probably be at the bottom of an uncapped dry oil well, and very hard to find, especially in a multidimensional generalization.) We have recently extended our fitting procedure so that it can be applied to moderate variation of our nonlinear parameters. There are good reasons to expect that this procedure

will lead to a considerably improved potential function that makes use of more suitable building blocks than we have hitherto used.

We had hoped to make many more computer runs using a suitable potential function. However, during some of these runs we detected unsuspected inadequacies of the then available potentials. Hence, we decided that we should postpone the extensive number crunching until we could arrive at a really good potential. The changes described above had to be included in our computer programs, which were already rather complex. We have made good progress on the rewriting and the necessary debugging, and are confident that we can soon arrive at the desired starting point for the production runs.

Nevertheless, the computer runs that we did make turned up some interesting phenomena. I will discuss the results obtained with a particularly simple potential, which made it possible to run the dynamical integrations much more quickly than with a realistic force. This potential had only central binary forces. The SF interaction was suitable for a description of the SF molecule. The FF interaction was taken from the F₂ molecule. The experimental normal mode (harmonic) frequencies for SFB₆S are 782, 649, 966, 620, 528 and 352 wave numbers, in the usual way of numbering modes. Our potential function gave instead the values 791, 852, 1247, 269, 260 and 153. The real equilibrium SF distance is 1.564 Å, while the model molecule had 1.540 Å. The total binding energy of the molecule is about 200 laser photons energy, while our result was 219. All in all, the agreement is surprisingly good. The resulting simple potential was used to test out and gain experience with the numerical integration of the Newtonian

equations of motion. The resulting data bank was used to make a moving picture of the molecular motion on 16 mm film. This film has been shown at conferences and lectures at a number of places: University of Illinois, Arizona State University, Los Alamos Scientific Laboratory, Oak Ridge National Laboratory, Lawrence Livermore Laboratory, University of California at Irvine, conference of Nobel Prize winners at Lindau in West Germany, and Fourth International Conference on Laser Spectroscopy at Rottach-Egern in West Germany.

One of the features of the film was that one saw vividly the enormous complexity of the motion. For the laser parameters used, one found typically that the molecule went rather quickly into the "quasicontinuum," and even well into the real continuum, long before it actually dissociated. From a study of distribution functions for kinetic energy values during the motion, we found that a meaningful "temperature" could be assigned to the single particle kinetic energies. The total energy of the molecule went up and down irregularly, but on the average it increased in a rather linear fashion in time. At the end of one run, the energy of the molecule had reached a value corresponding to the eventual escape of three F atoms.

There is considerable advantage to being able to characterize the very complicated motions by a few parameters of statistical distributions, such as the temperature. Otherwise, the required data storage will be enormous. Very likely, the effective temperature can be related to an evaporation rate which would mean that it would not be necessary to carry the numerical integration out nearly so far.

We hope to continue with this research project so that it can provide

an important method for getting insight into the mechanism of laser-induced molecular excitation and dissociation processes. These are important, not only for laser isotope separation, but also more generally for laser photochemistry and test laser photochemistry. A renewal proposal is being submitted to the Department of Energy.