

CALCULATIONS ON ISOTOPE SEPARATION  
BY LASER INDUCED PHOTODISSOCIATION OF POLYATOMIC MOLECULES

Final Report

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## ABSTRACT

This Progress Report describes research on the theory of isotope separation produced by the illumination of polyatomic molecules by intense infrared laser radiation. It is desired to investigate this process by integrating Newton's equations of motion for the atoms of the SF<sub>6</sub> molecule including the laser field interaction. The first year's work has been largely dedicated to obtaining a suitable interatomic potential valid for arbitrary configurations of the seven particles. This potential gives the correct symmetry of the molecule, the equilibrium configuration, the frequencies of the six distinct normal modes of oscillation and the correct (or assumed) value of the total potential energy of the molecule. Other conditions can easily be imposed in order to obtain a more refined potential energy function, for example, by making allowance for anharmonicity data.

We have also obtained a suitable expression for the interaction energy between a laser field and the polyatomic molecule. The electromagnetic field is treated classically, and it would be easily possible to treat the cases of time dependent pulses, frequency modulation and noise.

## 1. INTRODUCTION

This research involves a theoretical and numerical study of the dissociation of the SF<sub>6</sub> molecule in high power laser radiation by the method described in the proposal dated March 8, 1976. The object is to consider the polyatomic molecule SF<sub>6</sub> as a classical dynamical system obeying Newton's laws of motion, with forces on the atoms obtained from a suitable interatomic potential energy function. The laser radiation is able to exert forces on the atoms because they have effective charges which can be determined as indicated later. The real sulfur hexafluoride molecule should be described with the use of quantum mechanics. However, as was argued in the original proposal, it is expected that it is a very good approximation to treat the atomic dynamics classically. The only area in which much need for correction would be anticipated is in the early stages of the excitation process. Even there, if the motion were sufficiently harmonic it can be shown that no corrections are needed. However, the anharmonicity of the molecule does require some corrections to a classical calculation. Methods for making these were described in the proposal.

One of the big advantages of the classical approach is that we are always working in an inertial frame of reference. It is not necessary to transform to rotating axes fixed in the molecule. As a result, no centrifugal distortions, Coriolis forces or vibration-rotation interactions have to be considered separately. They are

built into the Newtonian dynamics. Once a suitable interatomic potential has been chosen, it is not necessary to consider the normal modes of vibration or the "radiationless transitions" between them which arise from the anharmonic forces. In the conventional "conversational" approach, much is said about the effect of "Rabi broadening," excitation up the "vibrational ladder," "leakage into the "quasi-continuum," "diffusion through the quasi-continuum" into the "real continuum" and ultimate dissociation. All of these things are automatically described quantitatively by the Newtonian equations of motion. We firmly believe that our approach offers the best possible method to get theoretical understanding of this very important problem for laser induced isotope separation and photochemistry.

One of the most interesting aspects of this problem is that it explores the borderline between the dynamical and statistical treatments of a technically important problem. No a priori assumptions about the applicability of unimolecular reaction theory are made. If such an approach turns out to be valid, the rate constants which are used in it will have been evaluated from first principles. The dynamical method is quite general and can be extended to many other polyatomic molecules.

In sections 2 - 6, we describe how the current  $SF_6$  potential is determined. Section 2 gives the initial approach in terms of a pair of Lennard-Jones potential functions with arbitrary coefficients. Section 3

develops a method for determining the potential constants given the experimental normal mode frequencies and equilibrium configuration. Limited to central forces, the method does not reproduce the SF<sub>6</sub> spectrum precisely. Section 4 succeeds in reproducing the spectrum by including three-body forces. The potential is accurate, however, only in the region about equilibrium. By specification of certain parameters such as the  $1/r^6$  F-F constant, and the total dissociation energy of the molecule, Section 5 yields a satisfactory global potential. Section 6 develops the laser-molecule interaction energy. Section 7 describes the computer facilities used in the project.

## 2. INITIAL FORMULATION

The SF<sub>6</sub> molecule has seven particles and twenty one Cartesian coordinates  $x_i$ ,  $i = 1, 2, \dots, 21$ . We first wrote a computer program LIS which allowed us to integrate the Newtonian equations of motion for the seven particles moving in a conservative potential energy field consisting of a sum of two body interaction potentials for the seven atoms. To get started, we took two potential energy terms for each of the 15 like particle pairs F-F: attractive ones varying as the inverse sixth power of the distances, and repulsive ones with inverse twelfth powers. We took two similar types of potential energy terms for each of the six unlike particle pairs S-F. In effect, we were introducing one Lennard-Jones potential for F-F (like) and another for S-F (unlike) particle pairs. The potential energy of the whole molecule could then be described by giving four constant coefficients  $B(1), \dots, B(4)$  to measure the strengths of the various types of interactions. At this stage, of course, we did not know the correct values for the four constants, and simply assumed them arbitrarily.

Our computer program LIS then sought out the equilibrium configurations for the molecule. It did this by starting from an arbitrary configuration and integrating the equations of motion of the particles with viscous damping introduced into their equations of motion in addition to the assumed interatomic forces. If the potential constants were suitably chosen, we found that there was an equilibrium configuration which had the desired octahedral symmetry.



Even if this were a stable equilibrium, it was not necessarily the one of lowest potential energy. However, by simple adjustments of the constants we could make the molecule have only the octahedrally symmetric equilibrium configuration.

We then applied the theory of small vibrations. The potential energy  $V(x_1, x_2, \dots, x_{21})$  needs to be expanded in a Taylor's series around the equilibrium configuration. The resulting matrix  $PV$  of  $21 \times 21$  second partial Cartesian coordinate derivatives plays a central role in the theory of small vibrations. Our computer program LIS calculated this matrix. It also found the eigenvalues and the similarity transformation matrix  $S$  which diagonalizes the  $PV$  matrix. The matrix  $S$  gives the relationship between the Cartesian coordinates and the normal mode coordinates. The 21 eigenvalues of  $PV$  are proportional to the squares of the frequencies of the normal modes of vibration of the molecule. (For the sake of a simpler discussion, we are overlooking the important fact that because the masses of the particles are not all equal to one another it is necessary to first transform from Cartesian to mass-normalized Cartesian coordinates before the making the matrix diagonalization.) As was to be expected, three of the eigenfrequencies came out to be zero corresponding to the three translational normal modes. Likewise, another three of the normal mode frequencies were zero corresponding to the three rotational normal modes. The remaining 15 nonzero vibrational frequencies showed the

degeneracies which are required by the octahedral symmetry of the molecule. Herzberg uses group-theoretical designations  $A_{1g}$ ,  $E_u$ ,  $F_{1u}$ ,  $F_{1g}$ ,  $F_{2g}$  and  $F_{1g}$  for these modes. Mode  $A_{1g}$  is non-degenerate and represents the highly symmetrical "breathing mode." Mode  $E_u$  is two-fold degenerate while the remaining modes are each three-fold degenerate. These normal modes are also designated by the numbers 1, 2, ..., 6 respectively. Modes 3 and 4 are the only optically active ones, and mode three is in close resonance with the radiation from a  $CO_2$  laser.

Naturally, since at this point we were only guessing the four potential constants, we obtained incorrect eigenfrequencies, but at least they showed the right pattern of degeneracies. It was almost inevitable that the equilibrium S-F distance would have the wrong value. This could easily be taken care of by rescaling distances. Our computer program also allowed a representation of the molecular configuration to be displayed on the screen of a CRT terminal (Tektronix 4013). We could start the motion off in some non-equilibrium configuration and watch the motion of the particles. Some of the motions seen in this manner were surprisingly complex. We also put into the program a rudimentary facility for having a periodic laser field exert forces on the particles. In this way, it was possible to demonstrate how the laser disturbed the motion. We did not follow up this approach very far because none of our constants were sufficiently realistic at this stage of

the work.

### 3. DETERMINATION OF CENTRAL FORCE POTENTIAL CONSTANTS

The next problem was to determine a set of potential constants for which the six eigenfrequencies would have the observed values, which in wave numbers are 782, 649, 966, 620, 528 and 352 for modes 1, 2, 3, 4, 5 and 6, respectively. At this point we had no idea how many potential energy constants  $B(i)$  had to be determined to specify the interatomic potential energy function. For any given potential, we could calculate the corresponding eigenfrequencies. The inverse problem of determining potential constants which would lead to the desired eigenfrequencies would be a formidable problem if approached in a direct manner. It would be very much like looking for a needle in an  $n$ -dimensional haystack where the number of dimensions  $n$  is unknown! Fortunately, however, we were able to devise a simple and effective method for dealing with this otherwise difficult problem. The computer program for doing this is called LISFIT.

In solving the problem of the  $21 \times 21$  matrix of second partial derivatives of the interatomic molecular potential function, the computer programs SIMTRAN and SIMEIGEN give the  $21 \times 21$  transformation matrix  $S$  between the Cartesian coordinate representation and the normal mode coordinates. It turns out that the form of this matrix is determined to an amazing degree by the high symmetry of the  $SF_6$  molecule.

The situation is somewhat analogous to what one

would have for the 2x2 matrix representing rotations in a plane about a fixed axis. All four elements of the rotation matrices are simply characterized by a single parameter representing the angle of rotation. In the case of the 21x21 matrix with which we are concerned, it turns out that all of the 441 elements are characterized by two parameters which we called alpha and delta. It is possible by a simple and systematic procedure to write down all of the elements of the transformation matrix. One can start by putting into the last three columns the numbers which intuitively correspond to the rotational modes, and into the next to last three columns the corresponding numbers for the three translational modes. The numbers which would represent the breathing mode can be put into the first column. From here on, one can proceed column by column, using a little intuition about what the normal modes might be, and making use of orthogonality conditions for pairs of columns and normalization for each column. Whenever one comes across a number which one does not know, it is denoted by some symbol. Most of these symbols can be determined in terms of others by using orthogonality conditions. In the end, one has only two unknown parameters delta and alpha remaining. The parameter alpha involves the doubly degenerate modes E and can be assigned arbitrarily without any loss of generality. The 3 and 4 modes are very similar (apart from being orthogonal!) to one another. Consider a triatomic linear complex F-S-F which lies along one of the Cartesian axes x, y or z. In equilibrium, the remaining four F atoms

lie at the corners of a square in a plane at right angles to the chosen axis. The square has the sulfur atom at its center. In both modes 3 and 4, all of the motions of the triatomic and of the square complexes are along such a chosen axis, the two F atoms on the axis move together, by equal amounts, and the modes differ only in respect to their differing relative motions of the S atom and the square array of F atoms. The ratios depend on  $\delta$ . Work at Los Alamos (kindly communicated by Dr. C. D. Cantrell) has determined the value of  $\delta$  by considering the observed rotational properties of the molecule, so we may regard it to be determined experimentally.

An equivalent expression of the previous paragraph would be to state that the secular equation of the  $21 \times 21$  matrix  $PV$  of partial derivatives of the potential energy function can be factored into 15 linear equations and three repeated sets of one quadratic equation for the normal mode frequencies. This factoring of the secular equation has been known since the 1930's, at least for the case of central forces, and we rediscovered it independently 40 years later.

The foregoing facts mean that we can determine the transformation matrix quite independently of what the potential energy function is, using only its octahedral symmetry properties. When the potential energy matrix is diagonalized, its six distinct nonzero elements are simply related to the normal mode frequencies of the molecule. These are known experimentally. This means that we can

transform the experimentally measured diagonal matrix in the normal mode representation "back" to the PV matrix of the Cartesian basis and thereby assign experimental values to all of the 441 elements. Suppose that the potential energy function is written down as a sum of elementary terms as we have described previously. For instance, for the like particles we would have a term of the attractive inverse sixth power van der Waals type. The function of distance is multiplied by a strength constant which might be denoted by  $B(1)$ . The  $21 \times 21$  matrix  $PV(1)$  of second partial derivatives can be calculated for this single potential energy term, and naturally all of its elements are dependent on  $B(1)$  in a linear fashion. The potential energy of the molecule would be a sum of such power law terms, each multiplied by its own strength coefficient  $B(i)$ . If the potential energy of the entire molecule, written as a sum of such terms, is differentiated with respect to each of the possible pairs of Cartesian coordinates of the 7 particles, we obtain the  $21 \times 21$  matrix PV of the theory of small vibrations, and the matrix is a sum of "influence" matrices  $PV(i)$  for the  $i$ -th elementary type of potential ingredient, each multiplied by the corresponding  $B(i)$ . We can then write down as many as 441 simultaneous algebraic equations for the  $B(i)$  which lead to a fit of the "experimental" matrix elements to the values calculated from the assumed force law. It turns out that of the 441 matrix elements associated with the potential energy function only eight are linearly independent of each other. In fact, there are eleven which

may have differing absolute values, but those three which are on the main diagonal are linear combinations of non-diagonal elements (an expression of the principle of conservation of linear momentum for the whole molecule.) With some thought one can be convinced that the numerology giving the number eight involves counting the six distinct nonzero normal mode eigenfrequencies, and adding one for translation and one for rotation. One can also conclude that it is not necessary to explicitly require that the molecule be in equilibrium at the chosen S-F distances. Information on the atomic spacing is already contained in the elements of the PV matrices. The fact that the PV matrix has zero rotational eigenvalue frequencies. implies, by a subtle argument, that the molecule is in equilibrium.

This means that we can write eight simultaneous linear algebraic equations to determine eight potential energy constants  $B(i)$  which are the strengths of the eight used types of elementary potential terms. The  $8 \times 8$  matrix of these simultaneous equations is denoted by GR. It has rows which refer to one of the eight independent elements of the PV matrix and columns which label the various potential types.

The foregoing discussion would suggest that we should take a potential energy function for the like particle pairs having inverse powers of  $r$  with exponents having values perhaps equal to 6, 7, 8 and 12 with a similar set for the unlike particle pairs. This would make a total

of eight potential energy constants  $B(1)$ ,  $B(2)$ , ... ,  $B(8)$ . One could then try to solve the eight simultaneous equations in the eight unknowns  $B(i)$  as described in the last paragraph. Unfortunately, the determinant of this  $8 \times 8$  GR matrix vanishes so that no meaningful solution could be obtained in this way.

One should, at this point, examine the elements of the  $8 \times 8$  GR matrix of the algebraic equations for determining the  $B$ 's in order to find out why the determinant vanishes. Inspection of the pattern of zeros and a little thought leads to the conclusion that a larger number of the distinct nonzero elements of the  $21 \times 21$  PV matrix are associated with like particle pairs than with unlike particle pairs. One can try to allow for this by taking more of the eight potential energy constants  $B(i)$  to refer to like particle pairs rather than to unlike particle pairs. This insight is helpful but not sufficiently so. The determinant still vanishes. The reason is that for the case of purely central force potentials between the particles, there is an equality between two of eight normally linearly independent elements of the PV matrix. This leads to a linear dependence of the eight "independent" elements of the PV matrix, and a zero determinant for the linear equations which must be solved for the  $B$ 's. A further consequence of the above equality of PV elements is that there is a simple linear relationship between the squares of three (1, 2 and 5) of the six normal mode frequencies. The existence of such a relationship can be seen in 1930 papers on  $SF_6$  which made use of harmonic



central forces. These had the relationship, but did not stress its importance. There were other early calculations which used non-central forces, and they did not lead to the algebraic relationship in question between the eigenvalues.

It was then clear that we had to have at least some non-central potential ingredient. Non-central forces have been used in the theory of the vibrations of polyatomic molecules for many years. Typically, one would introduce terms depending on the angles between adjacent bonds connecting atoms in the molecule. Such discussions are usually intended to deal with small excursions from equilibrium. In the work on the laser induced dissociation of polyatomic molecules it is very important to have a "global" potential which works well for arbitrarily large departures from equilibrium, since the ultimate object is to have the molecule dissociate. It therefore seemed important to us to have potentials which in the limit of large particle separations behaved correctly. For the case of two body potentials, this suggests that the inverse sixth power potential should dominate all others at large distance, since it is known that that is the correct asymptotic form of the van der Waals interaction. Naturally, if we had charged particles, Coulomb forces would be used. Even though there may be charges which can be assigned to the S and F atoms when they are close together, these charges will fall off exponentially with increasing separation, which will give a potential energy falling off asymptotically faster than with the inverse sixth power of the distance.

#### 4. INCLUSION OF THREE-BODY POTENTIALS

The next step in complexity beyond two particle interactions would be three particle ones. Consider three atoms at the corners of a triangle with sides  $a$ ,  $b$  and  $c$ , with the opposite angles denoted respectively by  $A$ ,  $B$  and  $C$ . In the limit of large distances there would be the usual dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, ..., etc. binary interactions. Subject to some assumptions, Margenau has shown additivity of these forces. There is a good discussion of non-additivity of van der Waals forces in the book by Margenau and Kessler. In addition, there will be genuine three body forces. The ones which appear in lowest order perturbation theory were first considered by Axilrod and Teller. The long range limit of the three body interaction potential is

$$(1 + 3 \cos A \cos B \cos C)/(a b c)^3.$$

This is the asymptotically dominant three-body interaction. There would, of course, be a whole sequence of other terms which would appear in higher orders of perturbation theory. These would be increasingly important for small values of  $a$ ,  $b$  and  $c$ . Because we wish to have a potential that works well at large separations, we have contented ourselves with non-central potentials of the kind considered by Axilrod and Teller.

At this point, we typically look for the like-particle binary interactions, the inverse powers 6, 7, 8 and 12, and for the unlike particle pairs 6 and 12. We brought the total number of interactions up to eight by

adding in an Axilrod-Teller term for like particle triplets F-F-F and another for unlike triplets S-F-F. We no longer had the difficulty of a vanishing determinant and a set of the  $B(i)$  could be determined. Usually, there would be something unpleasant about the indicated solution. For instance, although we would typically have an attractive inverse sixth power term for like particles, for unlike pairs it would be repulsive.

At this point the potential was doing everything we asked it to do (correct normal mode frequencies and degeneracies, correct equilibrium distances and correct value of the parameter  $\delta$ .) However, these things depend on the properties of the potential in a very limited region of the whole eight dimensional space of the  $B$ 's and it is not surprising that one of the inverse sixth power terms should have a physically unreasonable sign.

#### 5. SPECIFICATION OF CERTAIN POTENTIAL CONSTANTS

In order to get around this difficulty, we appealed to existing data on the SF and  $F_2$  molecules, and extracted (rough) values for the inverse sixth power terms. We then put these terms into our potential with the experimental coefficients. This "liberated" two more unknown  $B$ 's, so we added an inverse ninth power term for like particles and an inverse seventh power term for unlike particle pairs. Again we could get a good solution for the eight unknown  $B$ 's. This time we had the "right" inverse sixth power terms. However, typically, one of the inverse twelfth power terms was attractive. Not only that, but in

many cases the "pocket" in the potential energy function which corresponds to the small vibration analysis would be located on the steep side of a bottomless pit. We got around this difficulty by forcing in, by hand, a repulsive inverse twelfth power repulsion and made up the total of eight "unknown" B's by putting in another power law previously skipped over. Depending on the magnitude of the coefficient of the twelfth power term we found a potential with one or two equilibrium configurations. For a range of values of this coefficient we got a potential with reasonable properties. Ultimately, we will appeal to information on the anharmonicity of the potential in order to pick the "best" amount of the imposed inverse twelfth power repulsion. Of course, there is no fundamental theoretical reason for choosing the twelfth power. Lennard-Jones simply wanted to have some short range repulsion and happened to choose the exponent 12.

In order to further "tack down the potential function around the edges" we added another "experimental" quantity to the eight PV matrix elements presently being fitted: the total dissociation energy of the molecule. As a guess, this was taken to be six times the energy (about 30 mode 3 "photons") required to adiabatically remove one F atom from SF<sub>6</sub>. At this stage, we have a ninth type of force law with a strength coefficient B(9), and a 9x9 GR matrix.

Some general remarks on the search for a global potential are in order. It is clear from the usual

Born-Oppenheimer discussion that such a potential exists. It is also very unlikely that we can express it exactly in terms of a limited number of potential types. At most, we can hope to get a reasonably good approximation which reproduces a chosen set of experimental properties. We could lay more emphasis on the SF and F<sub>2</sub> two-body problems and begin with two-body terms which would really work for these molecules. We could let our nine (or more) unknown B's determine the admixture of three (and more) body force types. Presumably we would either use suitable generalizations of the Axilrod-Teller potential for higher orders of perturbation theory, or we could simply guess suitable functions (as has been done in recent work on three atom molecules.) We could have many more than nine such terms because we could not only require a fit of the normal modes of sulfur hexafluoride, but use whatever might be known of the other molecules with one sulfur atom and 2, 3, 4 and 5 fluorine atoms. Many other kinds of data could be used also, for example, isotope shifts. Such a program would be very worthwhile, but lengthy. It would be considerably simpler for a molecule like ammonia. The use of many three-body force terms would add enormously to the time required for integration of the dynamical equations of motion for the molecular dissociation. We think that for the main purpose of our project that we are already fairly near to a satisfactory global potential. It should be remembered that our two-body forces are designed to work in the SF<sub>6</sub> environment, and will not work so well in an

$F_2$ , SF,  $SF_2$  or  $SF_4$  environment. However, we will be interested to see how well they do. (We only used the long range inverse sixth power attractions for SF and  $F_2$ .) As a severe test of our "global" potential we can determine the equilibrium configurations and normal mode frequencies as well as the dissociation energies of  $F_2$  and all of the sulfur fluorides.

We close the discussion of the search for a molecular potential function with some more remarks of a general nature. We have given a number of lectures on this work (as at the Tenth International Quantum Electronics Conference in Atlanta in May, 1978.) It almost always happens that there is a question from the audience: Why do we try to get the interatomic potential in the way described? It is well known that there are very general computer "codes" for getting such potentials. It seems to us that this question misses some very important points. (1) It would enormously lengthen the dynamical calculations to proceed in the way suggested. (2) We would lose accuracy. No self-consistent field treatment of a 70 electron problem could possibly give potentials for the atoms with the precision of those which we borrow from the spectroscopic work. The resonance phenomena which make the project interesting require that good frequencies are put into the calculations. We do not believe that ab initio calculations could be sufficiently accurate. There would be more point in using them for a molecule about which very little was known. There also might be some utility for an

ab initio calculation of the long-range van der Waals coefficients, or an estimate of short range repulsions.

## 6. ELECTRIC FIELD-MOLECULE INTERACTION

We conclude with a brief discussion of how the interaction of the molecule with the laser radiation should be treated. Because the laser wavelength is much larger than the size of the molecule, the electric dipole approximation is a very good one. The laser radiation can be replaced by an oscillating spatially uniform electric field. Such a field exerts forces on the charged particles in the molecule. The interaction energy is a product of electric field and electric dipole moment of the molecule. A simple treatment would assign a negative charge to each F atom, and a positive charge of six times this much to the S atom. Then it would be a very simple problem to get the dipole moment of the molecule as a function of its configuration. (The dipole moment would be zero at equilibrium because of symmetry.) Because F atoms have a strong tendency to fill their 2p shell, it would be natural to think that the charge on the F atoms in sulfur hexafluoride would be closely equal to one electronic charge. Such an argument doesn't seem so strong when one wonders how the S atom feels about the loss of six electrons. In any case, the electrons are not localized on the nuclei. Our model requires forces on the atoms, and would become confused by a force on an extended electronic distribution. Fortunately, all we need to know is the expectation value of the dipole moment of the molecule for

any specified configuration of the nuclei. The product of this with the laser field gives a potential energy, and the force on any nucleus is obtained by taking a suitable vector gradient of the potential energy.

In principle, the dipole moment for any configuration of the nuclei could be given by an ab initio 70 electron calculation. For reasons analagous to those given before, we prefer to make use of experimental data and a little guesswork to get what we need for the dynamical calculations.

We assume that for any configuration of the molecule, the total electric dipole moment is a sum of dipole moments, one associated with each S-F bond. We assume that each S-F bond has a dipole moment along the bond, and a magnitude which is some function  $f(r)$  of the length  $r$  of the bond. We expect that  $f(r)$  falls off exponentially for large  $r$ , and that it vanishes for  $r = 0$ . Because of symmetry, the total molecule has a zero dipole moment in its equilibrium configuration. If the molecule is distorted by a mode 3 or mode 4 displacement, it acquires a dipole moment and the laser field can drive these modes.

We have applied this model to data on the optical absorption coefficient of the molecule for the 3 and 4 modes. This gives us the value of the function  $f(r)$  at the equilibrium S-F distance ( $1.564\text{\AA}$ ) and the derivative  $f'(r)$  at equilibrium. We then assume a functional form for  $f(r) = (a + br) r \exp(-r/D)$  with three constants  $a$ ,  $b$  and  $D$ . We



expect to guess that the decay distance  $D$  is about  $2\text{\AA}$ . The other constants in  $f(r)$  are determined from the intensity data on modes 3 and 4. The constant  $D$  could also be determined experimentally if measurements of transition strengths were available for the higher rungs on the vibrational ladders for the 3 and 4 modes.

## 7. COMPUTER FACILITIES

Our calculations are being made with a Data General ECLIPSE/230 minicomputer. This sixteen bit machine has 128K words of core and semiconductor memory (soon to be doubled with assistance from NSF), two 9-track 1600 bpi magnetic tape drives and a 192 megabyte disk storage system. (The help of ERDA in the acquisition of the last item was decisive, and has greatly enhanced the power of the whole facility.) We have a Megatek 6000 Graphics Display System which is refreshed by a DGC NOVA3/12 minicomputer linked to the ECLIPSE by a multiprocessor communications arrangement. There are also a Versatec 1200 line printer-plotter, a Tektronics 4013 storage scope terminal and a number of other terminals. An asynchronous line multiplexer supports an automatic answer line and seven other remote users. A dual drive diskette has just been added for convenient system and user file backup.

The ECLIPSE is a very fast and convenient computer. We have the new Advanced Operating System (AOS) which adds greatly to the power and flexibility of the facility. AOS is a multiprocess, multitasking system. Each user has access to his own files, and security against other users. He also has access to system utility files which can be used on a shared basis with other users. It is possible for the system manager to assign the rights and privileges of the various users in a very flexible way. Normally, any user process will acquire suitably chosen time slices, and each process can be swapped from core to disk, but it is possible

to create processes which are core resident and are never swapped out to disk. This means that certain processes can be largely immune to the presence of other users with less critical tasks. We have four batch streams, at least one of which can be made core resident. Hence a number of jobs associated with the LIS effort can be run simultaneously, and the computer will still be able to be useful to other people in the Optical Sciences Center. The FORTRAN 5 compiler is very efficient, and the language is a pleasure to use.

There are still a number of additional components which would make the system even more useful. Among these would be a DCU (Data Channel Unit) which would reduce the need for interrupts of the CPU by high speed terminals, a swapping disk to cut down time lost in swapping processes out to disk and an array processor which could enormously speed up our solutions of the differential equations of the dynamics of the SF<sub>6</sub> dissociation. We will need some kind of film producing facility in order to make communicable records of histories of the molecular dissociation process.

## COMPLIANCE

It is believed that the work reported represents reasonable compliance with the Contract requirements as stated in Appendix A of Contract No. EN-77-S-02-4294.

## PERCENTAGES OF TIME

The Principal Investigator expected to spend 8% of his time for 10 months and 100% of his time for 2 months in the year beginning July 1, 1977. In fact, he spent much more than 8% during the academic year. The budgeted summer compensation for 1978 could not be taken. Because of unexpected requirements for the computer, funds had to be shifted to provide a larger amount of time for a computer programmer's time. Nevertheless, the above time commitment for the summer months has been satisfied.

## OTHER SCIENTIFIC PERSONNEL

Murray Sargent III, Professor of Optical Sciences

Lionel N. Menegozzi, Visiting Associate Professor  
of Physics and Research Associate

Bruce J. DaCosta, Computer Programmer