Lawrence Berkeley National Laboratory
Recent Work

Title
STUDIES OF MULTIPHOTON DISSOCIATION OF POLYATOMIC MOLECULES WITH CROSSED LASER AND MOLECULAR BEAMS

Permalink
https://escholarship.org/uc/item/2001q68h

Author
Grant, E.R.

Publication Date
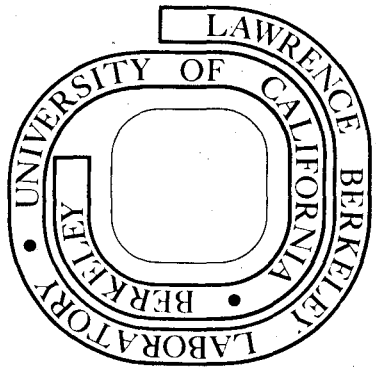1977-05-01

U J J J 4 7 i i 3 i 2

STUDIES OF MULTIPHOTON DISSOCIATION OF POLYATOMIC MOLECULES WITH CROSSED LASER AND MOLECULAR BEAMS

E. R. Grant, M. J. Coggiola, Y. T. Lee, P. A. Schulz,
Aa. S. Sudbo, and Y. R. Shen

May 1977

LAWRENCE UNIVERSITY OF CALIFORNIA BERKELEY LABORATORY

DISCLAIMER

STUDIES OF MULTIPHOTON DISSOCIATION OF POLYATOMIC MOLECULES WITH CROSSED LASER AND MOLECULAR BEAMS

E.R. Grant, M.J. Coggiola[*] and Y.T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California, Berkeley, CA 94720

P.A. Schulz, Aa.S. Sudbo, and Y.R. Shen

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Physics
University of California, Berkeley, CA 94720

Recently, collisionless multiphoton dissociation (MPD) of polyatomic molecules by infrared lasers has become one of the most interesting and exciting problems in quantum electronics and laser chemistry ([1]). The process is isotopically selective and provides a potentially effective and inexpensive method for isotope separation ([2]). It has also been suggested that MPD could lead to mode-selective bond breaking ([3]). If this were indeed the case, the process would have a revolutionary effect on photochemical synthesis and other areas of chemistry.

From the scientific point of view, MPD is also an extremely intriguing problem. In order to reach the dissociation threshold, a single molecule has to absorb several tens of infrared photons. This is a nonlinear process. Usually, even a 3- or 4-photon absorption process would require a laser beam intensity of the order of MW/cm^2 or higher. For absorption of several tens of photons simultaneously, one would expect to take a laser intensity close to the gas breakdown threshold, namely, ~ 10 GW/cm^2 or more. Therefore, it was quite surprising when it was found that only a laser intensity of ~ 10 MW/cm^2 or a pulse energy of ~ 1 J/cm^2 is needed for MPD ([4],[5]). Then, the questions which must be answered are why can a single molecule absorb so many photons of same frequency with a large probability, how many photons are actually absorbed per molecule, how is the absorbed energy distributed in the excited molecule before dissociation, and what is the subsequent dynamics of dissociation. Here, we would like to discuss how we can answer most of these questions quantitatively from our recent molecular beam studies on MPD ([6]).

There already exists in the literature a large number of reports on the experimental and theoretical studies of MPD ([1],[7]), and some of the questions related to the absorption have been answered. The techniques used in the experiments are, however, limited. In almost all cases, CO_2 TEA laser pulses were used to excite the low-pressure gas medium in a sample cell. One would make 1000 or 2000 laser shots ([8]) and analyze the gas medium

before and after the shots by optical absorption and mass spectroscopy. If possible, the induced luminescence in the medium was also monitored during the shots. The measurements were carried out as a function of laser power, energy, frequency, pulsewidth, gas pressure, gas mixtures, etc. An obvious difficulty of such experiments is that the observation of the dissociation process is always influenced by molecular collisions and chemical reactions following the laser excitation. Consequently, interpretation of the results is often uncertain, confusing, and sometimes even inconsistent. Direct, quantitative information about the dynamics of MPD is difficult to obtain. For example, such experiments sometimes cannot even tell for certain what the primary dissociation fragments are and how many infrared photons per molecule dissociated are absorbed. Then, the results on the dependence of MPD on laser power, energy, frequency, etc. can all be affected by molecular collisions and chemical reactions.

It is clear that in order to fully understand MPD one must try to avoid molecular collisions. With this in mind, the Harvard group has used subnanosecond CO_2 laser pulses much shorter than the mean free time between molecular collisions to study MPD in a gas cell (5). However, even though the laser excitation time is short, the dissociation lifetime of a molecule can still be longer than the collision time, and hence their results of MPD are still more or less affected by molecular collisions. It seems to us that the only way to eliminate molecular collisions in the studies of MPD is to use a molecular beam. A molecular beam experiment on CO_2 laser-induced dissociation of SF_6 was performed previously by Brunner et al., (14) in which the influence on the molecular beam of SF_6 itself by the CO_2 laser was studied using the mass spectrometer. In our experiments, using a rotatable mass spectrometer, direct identification of fragment species as well as the measurements of angular and velocity distributions of dissociated products were performed for the understanding of the dynamics of excitation and dissociation.

Experimental Arrangement

Our experimental setup is shown schematically in Fig. 1 (6). The molecular beam was a supersonic jet from a 0.1 mm nozzle. The beam diameter at the collision center was about 2 mm with a divergence angle of 0.8°. At 75-torr stagnation pressure, the molecular density in the beam was $\sim 3 \times 10^{11}$ cm^{-3}. The laser was a Tachisto CO_2 TEA laser putting out about 0.5 - 1 J/pulse. A 25-cm ZnSe lens was used to focus the laser beam. The two beams crossed at the collision center and the dissociation fragments from the collision region were then analyzed by a detector which consisted of an ionizer, a quadrupole mass spectrometer, and a gated counting system. The detector could be rotated with respect to the collision center so that the angular distribution of the fragments could be measured. The angular resolution was better

than ± 0.5°. At a given angle, the velocity distribution of the fragments could also be obtained from the time-of-flight measurement. The pressure in the collision chamber was about 5×10^{-7} torr and that of the ionization chamber of the detector was about 10^{-10} torr.

Experimental Results and Discussion

What have we learned from our experiment? We shall discuss mainly MPD of SF_6 since most of our experiments were done with this molecule. First of all, we found that the dissociation fragments could be readily detected and at high laser pulse intensities or energy densities, the signal appeared to be saturated indicating that almost all excited molecules in the beam were dissociated. This result constitutes a direct proof to the collisionless nature of MPD. That MPD can occur with large probability at not very high laser intensities has been the subject of many recent theoretical papers (1,9). It is now qualitatively understood as due to the following physical mechanism (10).

In order that a single molecule can absorb several tens of photons from a monochromatic laser beam with high probability, each one-photon transition step in the multiphoton excitation process must be resonant or nearly resonant. This would be possible if molecular vibration were strictly harmonic. In practice, however, the anharmonicity in a vibrational mode is always so large that no resonant stepwise excitation up the pure vibrational ladder can happen. Fortunately, the energy level diagram of a polyatomic molecule is more complicated. Superimposed on the vibrational levels, there are numerous rotational levels. In addition, the degeneracy of the excited vibrational levels can be lifted by Coriolis coupling and by anharmonic coupling with other modes. As a result, starting from a range of rotational levels in the ground vibrational state, it is possible to have the first 3-6 one-photon stepwise excitations nearly resonant up the rotation-vibrational ladder. Then, the density of states of a polyatomic molecule always increases rapidly with energy and soon the energy levels form a quasi-continuum. For example, the density of states of SF_6 at 5000 cm^{-1} is already as high as $10^3/cm^{-1}$ (10). Thus, after the first 3-6 stepwise one-photon excitations, the laser field essentially interacts with a continuum of states, and the subsequent individual steps in the stepwise multiphoton transition through the quasi-continuum to and beyond the dissociation limit are all "resonant." This then qualitatively explains why a relatively low infrared laser power or energy is sufficient for MPD of polyatomic molecules.

The second important aspect of our experiment was that we could identify the dissociation fragments before they undergo secondary collisions with other molecules on the wall. However,

the identification of the fragments of SF_6 is much more compli-
cated than what we stated erroneously in our previous work (6).
Sulfur polyfluorides are known to decompose almost completely in
the ionization process into daughter ions. It was found that the
ratio of SF_3^+/SF_2^+ is a much more reliable way of identifying
products. We found that the primary dissociation products are
SF_5 + F. This is in fact what one would expect from the energy
consideration since SF_5 + F is the lowest dissociation channel.
It has a dissociation threshold at 77 KCal/mole as compared to
that of SF_4 + F_2 at 105 KCal/mole. Previous experiments by
others had suggested that SF_4 and F_2 were the dissociation frag-
ments (11). It turns out that SF_4 could actually appear as a
secondary dissociation product when the laser energy is increased.
No F_2 signal was ever detected. These results suggest a two-step
mechanism for the production of SF_4:

$$SF_6 + nh\nu \xrightarrow{\ \tau\ } SF_5^* + F$$

$$+$$

$$n'h\nu$$

$$\xrightarrow{\ \ } SF_4^* + F$$
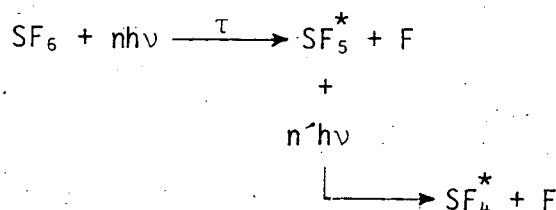
where τ indicates the average dissociation lifetime and * denotes
internal excitation. Clearly, the laser pulse width, $T \geq \tau$ in
order for the second dissociation step to be significant. Our
results therefore suggest that average τ must be close to or less
than the laser pulse width of 50 nsec.

As we mentioned earlier, our apparatus also allowed us to
measure the angular distribution and velocity distribution of the
fragments. An example is shown in Fig. 2. Such results together
with the velocity distribution of the primary beam could yield
quantitative information about the dynamics of dissociation.
Let $\vec{v}_0$ and $\vec{v}$ be the velocities of the primary beam and the frag-
ment respectively, and ⊕ be the angle between $\vec{v}_0$ and $\vec{v}$.
Let $f(v, ⊕)$ be the fragment velocity distribution at ⊕, $h(v_0)$ be
the velocity distribution of the primary beam, and $g(u = |\vec{v} - \vec{v}_0|, \theta)$
be the fragment velocity and angular distribution in the center of
mass coordinates. We first observed qualitatively that the
angular distribution is isotropic in the center of mass coordi-
nates so that $g(\vec{u}) = g(u)$. This was true for at least the case
of SF_6 since our experimental results also showed no dependence
on the laser polarization. We then have

$$f(v, ⊕) = \int g(u = |\vec{v} - \vec{v}_0|)h(v_0)dv_0$$

from which we can deduce $g(u)$ by deconvolution if $f(v,\theta)$ and $h(v_0)$
are known from measurements. The recoil kinetic energy $\mathcal{E}$ of the
fragments is given by $\mathcal{E} = \frac{1}{2} m_f u^2$, so $g(u)$ can be readily trans-
formed into the fragment recoil-energy distribution $g(\mathcal{E})$. In
Fig. 3, we show an example of $g(\mathcal{E})$ obtained with laser pulses of

-4-

~ 50 nsec in pulsewidth and ~ 6 J/cm^2 in energy. Theoretical curves are also shown for comparison.

Before we discuss the theoretical calculation of $g(\mathcal{E})$, we should point out that three qualitative but important conclusions can readily be drawn from the experimental data. (1) The fragment angular distribution in Fig. 2a suggests and the fragment recoil-energy distribution in Fig. 3 confirms that the average recoil energy of the fragments is low, approximately 2-3 KCal/ mole which is about a CO$_2$ laser photon per molecule. This indicates that if SF$_6$ before dissociation absorbs many more than one photon above the dissociation level, a large fraction of this excess energy must be retained by the SF$_5$ fragment in its internal degrees of freedom. (2) If the dissociation has an appreciable exit barrier energy, then the fragment angular distribution would peak at $\theta \neq 0$ and the fragment recoil-energy distribution would correspondingly peak at $\mathcal{E} \neq 0$. This is apparently not the case for SF$_6$ as seen in Fig. 2a and Fig. 3, indicating that the barrier energy for SF$_6 \rightarrow$ SF$_5$ + F is essentially zero or less than 0.2 KCal/mole. (3) If MPD is mode-selective, a velocity distribution skewed to higher energy would be expected. Figure 3 shows that this is not the case for SF$_6$. The strong peaking of product molecules at zero kinetic energy is exactly what is expected if the energy in the excited molecule is completely randomized before decomposition.

We now discuss how we can deduce more quantitative information about MPD by comparing theory and experiment on $g(\mathcal{E})$. We believe that because of the very strong coupling among various vibrational modes at high excitations, the excitation energy deposited in the molecule should be randomly distributed in all vibrational degrees of freedom. We can therefore use the RRKM statistical model for unimolecular dissociation (12) to calculate $g(\mathcal{E})$. The model assumes that a molecule is initially excited to an energy level E (or statistically to many levels with a certain distribution) above the dissociation energy E$_0$, and that the excitation energy is randomly distributed in all composite vibrational states. If N$_E$ is the density of vibrational states of the molecule at E, and G$_E(\mathcal{E})$ is the density of states in which the excited molecule will sooner or later dissociate with a fragment recoil energy $\mathcal{E}$, then the probability that the molecule will dissociate with a recoil energy is

$$P_E(\mathcal{E}) = G_E(\mathcal{E})/N_E$$

and hence the fragment recoil-energy distribution is given by

$$g_E(\mathcal{E}) = P_E(\mathcal{E})/\int_0^{E-E_0} P_E(\mathcal{E})d\mathcal{E}.$$

For a given molecule, N_E and $g_E(\mathcal{E})$ can be obtained from model calculation. Therefore $g_E(\mathcal{E})$ [or $g(\mathcal{E})$ for excitation distributed over many levels] can be calculated and compared with the experimental data. In addition, the dissociation rate $k_E(\mathcal{E})$ which is proportional to $P_E(\mathcal{E})$ can also be obtained from the model calculation knowing $P_E(\mathcal{E})$. The total dissociation rate of the molecule is given by

$$K_E = \int_0^{E-E_0} k_E(\mathcal{E}) d\mathcal{E}$$

and the corresponding dissociation lifetime is $\tau_E = 1/K_E$.

Figure 3 shows three $g_E(\mathcal{E})$ curves calculated by assuming $E = n\hbar\omega$ with $n = 7, 9,$ and 11, where $\hbar\omega$ is the CO_2 laser photon energy. The $n = 9$ curve clearly fits well with the experimental date. Actually, there is a significant spread in the levels of excitation for a given laser energy, $n = 9$ merely means the average level of excitation. The agreement between theory and experiment leads to the following conclusions:

(1) The RRKM statistical model for unimolecular dissociation assuming random energy distribution in all vibrational degrees of freedom gives a correct description of the dynamics of MPD. The mode-selective dissociation is clearly not possible for at least MPD of SF_6 with nanosecond pulsed excitation.

(2) For MPD of SF_6, the molecule mostly likely dissociates from a level at 7 to 11 $\hbar\omega$ above E_0 depend on laser energies. In other words, since $E_0 \simeq 29 \hbar\omega$, each SF_6 molecule actually absorbs on average 36 to 40 infrared photons before dissociation. This should be compared with the estimate of 200-250 photons reported earlier in the literature (13).

(3) The calculated dissociation rates versus $E - E_0 = n\hbar\omega$ for SF_6 are shown in Fig. 4. We find that for $n = 7$ to 11, the corresponding dissociation lifetime is ~ 50 to 0.5 nsec. This is in the same order of magnitude as laser pulsewidths.

(4) Figure 4 shows that the dissociation rate increases rapidly with n. This explains why the dissociated molecules appear to have originated from an energy level $E = E_0 + 7 \hbar\omega$. For $E < E_0 + 6 \hbar\omega$, the up-excitation rate is much larger than the dissociation rate and hence only a small fraction of molecules in these levels can dissociate. For $E > E_0 + 11 \hbar\omega$, the dissociate rate is much larger than the up-excitation rate and only a small fraction of molecules can be excited to higher levels. The results also suggest that over a wide range of laser powers, the level of excitation would not vary significantly. This was found to be the case in SF_6.

We have also performed a number of other measurements of MPD. Limited by space here, we will only discuss briefly some of them:

(1) We have measured for MPD of SF_6 the dependence of the fragment intensity as a function of laser power and energy. The threshold energy (defined by the limit of our detection sensitivity) was around $2J/cm^2$ and appeared to be the same for laser

pulsewidths of 50 nsec and 500 nsec. For 500-nsec pulsewidth, this energy threshold corresponds to a power threshold of ~ 4 MW/cm^2 which is 6 times lower than the earlier reported value (4). For longer pulses, the power threshold could be even lower. This suggests that the energy threshold is probably more meaningful even though MPD must also depend on the laser peak power in some way. Above the threshold, the fragment intensity increased almost linearly and then quickly leveled off to saturation at ~ 10 J/cm^2. These results obtained under the strict collisionless condition should form the basis of any quantitative theory on MPD. With increasing laser energy, the fragment angular distribution first became somewhat broader. Then, above 15 J/cm^2, it remained essentially unchanged, indicating that it was difficult to excite the SF$_6$ molecules to $E - E_0 > 11\ \hbar\omega$.

(2) We have measured the excitation spectrum for MPD of SF$_6$. Compared to the one reported earlier by Ambartzumian et al (4), our spectrum had a full width of ~ 12 cm^{-1} instead of 19 cm^{-1} and a peak shifted from the Q branch by ~ 4 cm^{-1} instead of 8 cm^{-1}. In both cases, the vibrational temperatures and laser energies are supposed to be the same, but the vibrational temperature of the molecules in the gas cell experiments could become somewhat hotter during the experiment.

(3) We have found that MPD of SF$_6$ does not depend on the laser polarization. This indicates that the excitation energy is distributed isotropically in the rotational substate or/and the dissociation lifetime is much longer than the rotational periods.

(4) We have also made preliminary measurements on MPD of a number of other molecules, e.g., CF Cl$_3$ and CF$_3$Br. In all cases, the dissociation occurred through the lowest dissociation channel, indicating that the statistical model for MPD discussed earlier for SF$_6$ should also be applicable to other polyatomic molecules.

Concluding Remarks

In summary, we have shown that through molecular beam studies, we have learned a great deal about excitation and dissociation processes in MPD. Specifically, we have been able to identify the dissociation products, to learn about the excitation energy distribution in the excited molecule, to determine the level of excitation before dissociation, and to find the dissociation rate and lifetime. We have concluded that the RRKM statistical model for unimolecular dissociation gives a good description of the dynamics of MPD, and that the possibility of a mode-selective explosive type of MPD can be ruled out. There are, of course, many other experiments yet to be done in rigorously collisionless conditions of molecular beam in order to further our understanding on MPD. For example, we should measure MPD by varying the laser pulsewidth over a wide range, by using two exciting laser pulses with different energies and frequencies and a time delay between

them, and by heating and cooling the rotational and vibrational degrees of freedom of the molecular beam. These experiments are presently being carried out in our laboratory.

ABSTRACT

It is shown that our crossed laser and molecular beam studies of collisionless multiphoton dissociation of polyatomic molecules have led to a much better understanding of the dynamics of excitation and dissociation of this important isotopically selective process.

Literature Cited

*Present address: Stanford Research Institute, Menlo Park, CA.

(1) See, for example, papers in "Tunable Lasers and Applications," Proceedings of the Nordfjord Conference, edited by A. Mooradian, T. Jaeger, and P. Stokseth, (Springer-Verlag, 1976), and references therein.

(2) Ambartzumian, R.V., Letokhov, V.S., Ryabov, E.A., and Chekalin, N.V., JETP Lett. (1974) 20, 273; Lyman, J.L., Jense, R.J., Rink, J., Robinson, C.P., and Rockwood, S.O., Appl. Phys. Lett. (1975) 27, 87.

(3) Denver, D.F. and Grunwald, E., J. Am. Chem. Soc. (1976) 98, 5055.

(4) Ambartzumian, R.V., Fuzikov, N.P., Gorokhov, Yu A., Letokhov, V.S., Marakhov, G.N., and Puretzky, A.A., Optics Comm. (1976) 18, 517.

(5) Kolodner, P., Winterfeld, C., and Yablonovitch, E., Optics Comm. (1977) 20, 119; Black, J.G., Yablonovitch, E., Bloembergen, N., and Mukamel, S. (to be published).

(6) Coggiola, M.J., Schulz, P.A., Lee, Y.T., and Shen, Y.R., Phys. Rev. Lett. (1977) 38, 17; Grant, E.R., Coggiola, M.J., Lee, Y.T., Schulz, P.A., and Shen, Y.R., Chem. Phys. Lett. (to be published).

(7) See, for example, review articles by Letokhov, V.S. and Moore, C.B., Sov. J. Quantum Electronics (1976) 3, 259 [English translation: Kvantovaia Elektronika (1976) 3, 485]; Lyman, J.L. and Rockwood, S.D., Proc. Conference on Lasers and Electro-Optics, Anaheim, Calif. (Nov., 1975) (to be published) and references therein.

(8) Recently, Gower, M.C. and Billman, K.W. [Optics Comm. (1977) 20, 123] have claimed that they could observe multiphoton dissociation of SF_6 with a single laser shot in a gass cell.

(9) See, for example, Stones, J., Goodman, M.F., and Dows, D.A., J. Chem. Phys. (1976) 65, 5062; Mukamel, S. and Jortner, J., J. Chem. Phys. (1976) 65, 5204; Cotter, T.P., J. Chem. Phys. (to be published).
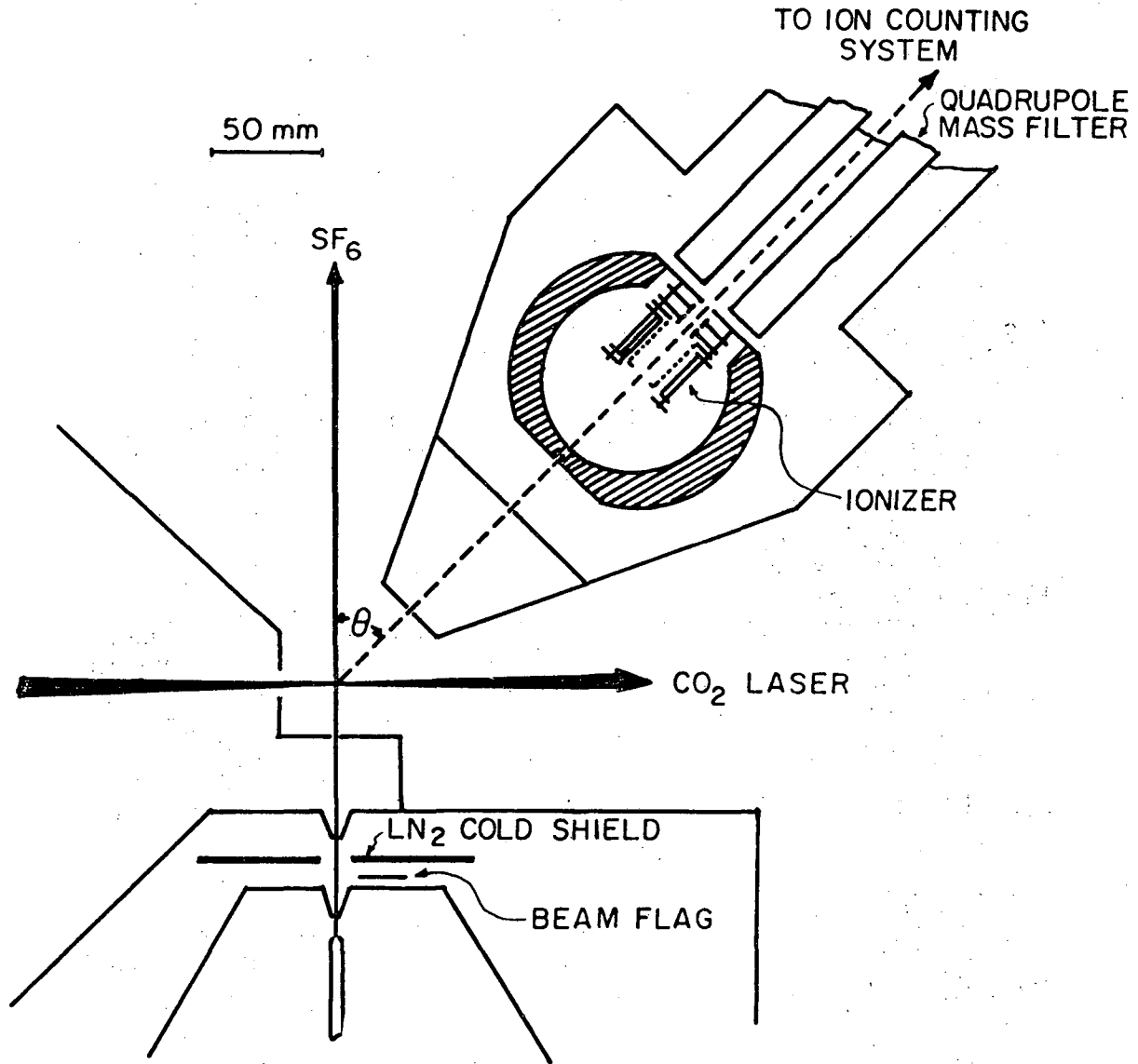
(10) Larsen, D.M. and Bloembergen, N., Optics Comm. (1976) 17, 254; Letokhov, V.S. and Makarov, A.A., Optics Comm. (1976) 17, 250; Mukamel, S. and Jortner, J., Chem. Phys. Lett. (1976) 40, 150; Hodgkinson, D.P. and Briggs, J.S., Chem. Phys. Lett. (1976) 43, 45.

(11) Kompa, K.L. in Ref. 1, and also paper given at the Laser Chemistry Conference, Steamboat Springs, Colorado (1976).

(12) See, for example, Robinson, P.J. and Holbrook, K.A., "Unimolecular Reactions" (J. Wiley, New York, 1972).

(13) Ambartzumian, R.V., Gorokhov, Yu A., Letokhov, V.S., Makarov, G.N., Ryabov, E.A. and Chekalin, N.V., Sov. J. Quantum Electron. (1976) 6, 437.

(14) Brunner, F., Cotter, T.P., Kompa, K.L., and Pruch, D., J. Chem. Phys. (in press).

Figure Captions

Fig. 1. Schematic of the apparatus for studies of multiphoton dissociation of SF_6. The molecular beam is triply differentially pumped.

Fig. 2. (a) Angular distribution of the SF_3^+ fragments from multiphoton dissociation of SF_6.
(b) Flight time distribution of the SF_3^+ fragment. The narrow angular distribution and longer flight times ● are indicative of SF_5 at a laser energy density of ~ 6 J/cm^2. The wider angular distribution and shorter flight times ■ are indicative of SF_4 at a laser energy density of ~ 15 J/cm^2. The angular distribution ▲ was obtained at a laser energy density of ~ 50 J/cm^2.

Fig. 3. Fragment recoil energy distributions for $SF_6 \rightarrow SF_5 + F$. Experimental data points obtained with ~ 6 J/cm^2 laser pulses are denoted by ●. Curves are calculated from the RRKM theory assuming a molecular excitation of $E = E_0 + n\hbar\omega$ with $n = 7(— \cdot —)$, $n = 9(—)$, and $n = 11(----)$ where E_0 is the dissociation energy and $\hbar\omega$ is the CO_2 laser photon energy.

Fig. 4. Dissociation rate of SF_6 calculated from the RRKM theory as a function of level of excitation $n\hbar\omega = E - E_0$.
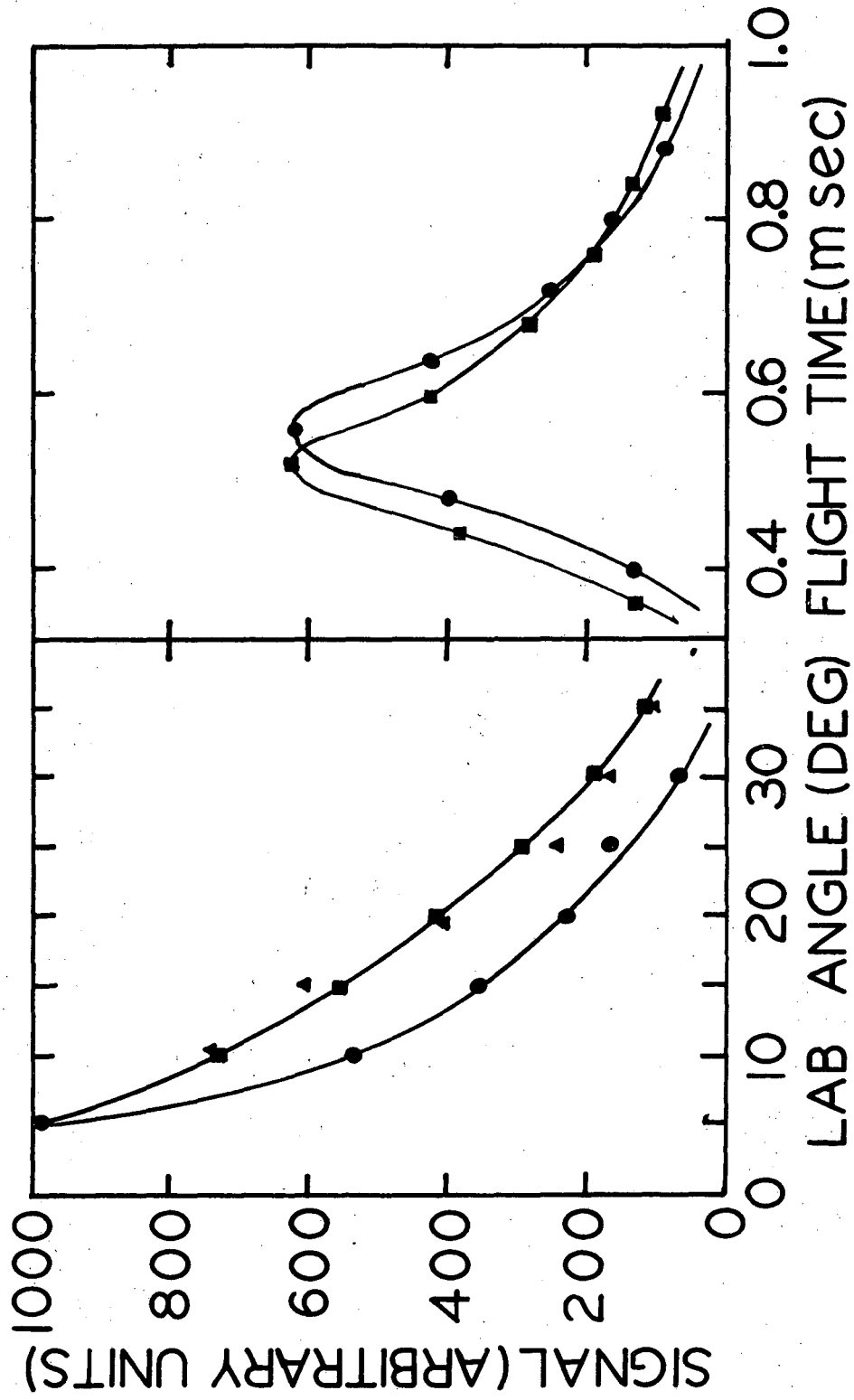
Acknowledgment

TO ION COUNTING
SYSTEM

QUADRUPOLE
MASS FILTER

50 mm

SF$_6$

IONIZER

θ

CO$_2$ LASER

LN$_2$ COLD SHIELD

BEAM FLAG

XBL 768-10162

Fig. 1

XBL 771-7433

Fig. 2

Fig. 3

XBL 771-7431

Fig. 4

XBL775-5448