Lawrence Berkeley National Laboratory

Recent Work

Title

PHOTOIONIZATION STUDY OF MULTIPHOTON EXCITED SF₆ IN A MOLECULAR BEAM

Permalink

<https://escholarship.org/uc/item/2cg9s7s3>

Author

Sudbo, As.S.

Publication Date

1979-03-26

PHOTOIONIZATION STUDY OF MULTIPHOTON EXCITED SF₆
IN A MOLECULAR BEAM

RECEIVED
LAWRENCE
BERKELEY LABORATORY Aa. S. Sudbø, P. A. Schulz, D. J. Krajnovich,
Y. T. Lee and Y. R. Shen

MAR 23 1979

February 1979

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782*

LBL-8765a.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

PHOTOIONIZATION STUDY OF MULTIPHOTON EXCITED SF₆
IN A MOLECULAR BEAM

Aa. S. Sudbo^a, P. A. Schulz^a, D. J. Krajnovich^b,
Y. T. Lee^b and Y. R. Shen^a

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

FEBRUARY 1979

ABSTRACT

We have used a molecular-beam photionization technique to probe the vibrational energy distribution of SF₆ molecules excited by an intense CO₂ laser at energy fluences close to and below the dissociation threshold. We observe a significant "bottleneck" at low laser intensities. Even at laser fluences close to the dissociation threshold, most of the molecules remain in the discrete levels, and only a small fraction (< 20%) is excited into the quasi-continuum.

^aAlso associated with the Department of Physics, University of California, Berkeley.

^bAlso associated with the Department of Chemistry, University of California, Berkeley.

Infrared multiphoton dissociation of polyatomic molecules has turned out to provide a new meeting ground for physicists and chemists.¹ One of the questions that has received considerable attention recently by both physicists and chemists is: What does the population distribution of multiphoton-excited molecules over their internal energy states look like? Numerous theoretical²⁻⁵ as well as experimental⁶⁻⁹ works have been reported, yet no conclusive agreement has been reached on how the population distribution should best be modeled.

For sufficiently high laser intensity and energy fluences, it is well established^{1,10} that close to 100% of the irradiated molecules can dissociate. Then it seems reasonable to use a picture that as the laser excites the molecules, the population distribution becomes a bell shaped function of the excitation energy, and the average excitation energy increases with the increase of laser energy fluence. Both the thermal model^{1a,6b} and the rate equation approach^{2,3} agree qualitatively with this picture, and have been successful in describing the experimental results on the dissociation yield and average energy absorbed as a function of laser fluence for SF_6 . However, for sufficiently low laser intensities it is believed that because widely different laser intensities are needed to excite molecules initially in different rotational states over the discrete levels to the so-called quasi-continuum,¹ only a small fraction of the molecules can actually be excited into the quasi-continuum. This can be concluded from the observation that the average number of photons absorbed by SF_6 for the same laser

fluence depends strongly on the intensity of the laser when the laser fluence is low.¹¹ At a given laser frequency and power level, only molecules in certain vibration-rotation levels can interact in resonance or near resonance with the laser field, and get excited to the quasi-continuum by absorbing 3 or 4 photons.

So far, few and conflicting experimental results have been reported on the laser intensity needed at a given frequency to excite an appreciable fraction of a given molecular species. Double resonance⁷ and energy absorption⁸ measurements on SF_6 , C_2H_4 , CH_3F and SiF_4 suggest that regardless of initial rotational state, most molecules are excited into the quasi-continuum at laser intensities well below those needed to observe dissociation. However, two frequency dissociation yield measurements by Ambartzumian et al.⁹ on the molecule OsO_4 indicate that, at comparable laser intensities, only a small fraction of the molecules are excited into the quasi-continuum. The experiments reported here, using a photoionization method to detect the excited molecules, show that the same is true for SF_6 , contrary to the conclusions reached by Alimpiev et al.⁷ and Akhmanov et al.⁸ At laser energy fluences close to or below the dissociation threshold, with a pulse duration of 250 nsec, only a small fraction (< 20%) of the molecules seem to have absorbed much more than 2 or 3 photons of energy from the laser field.

The experimental setup shown in Fig. 1 is a modification of the molecular beam photoionization apparatus described in detail elsewhere.¹²

A well collimated SF_6 molecular beam was crossed, in a 0.3 - 1.0 cm long region, centered 3.3 cm upstream from the photoionization region, by 0.3 - 0.4 J multimode pulses from a Gen-Tec DD-250 line-tunable CO_2 TEA laser. The pulses had a FWHM of 250 ns (measured with a photon drag detector), and had a repetition rate of 100 Hz. The laser output was focused by a 10" focal length ZnSe lens, and the intensity of the laser pulse was varied by adjusting the distance of the lens away from the beam. This also affected the length of the interaction region where the beam crossed with the laser. After irradiation by the CO_2 laser, the molecular beam was crossed and ionized by a vacuum UV beam from a pulsed He lamp, dispersed through a 1 m vacuum UV monochromator with 0.25 nm resolution. The photoions produced were extracted from the ionization region by electrostatic ion lenses, and focused into the entrance slit of a quadrupole mass spectrometer. The mass selected photoions arriving at a Daly type detector were then counted. In the present experiment, we studied the photoionization spectrum of SF_6 by the detection of SF_5^+ ions, by far the most abundant ions produced, via the process $\text{SF}_6 + h\nu_{\text{UV}} \rightarrow \text{SF}_5^+ + \text{F} + e^-$.¹³

The spectra were taken by a microprocessor-controlled gated counting and UV frequency-scanning system. Three gated scalars were used, counting respectively photoions with SF_6 irradiated, photoions from SF_6 without irradiation, and a photoelectric signal proportional to the UV light intensity. The raw spectra were then analyzed in the

way explained below. Each spectrum scan typically took three to five hours. The molecular beam intensity was stable over long periods of time; the laser had a better than 10% pulse-to-pulse reproducibility, and the long term drift in power output was less than 20%. The laser fluences at the molecular beam were estimated from the measurement of the total pulse energy and the area irradiated.

Because the molecular beam had a velocity spread, and there was a time delay between laser irradiation and photoionization, only a certain fraction of SF_6 subjected to photoionization during the "laser on" counting period actually came from laser irradiated molecules. From the measured time-of-flight distribution of the beam, and the given experimental parameters (scaler gate width and delay, and length of the section of molecular beam being irradiated by the laser), this fraction, f , can be calculated, as tabulated below for the three laser energy fluences used in the experiment.

<u>Laser Energy Fluence (J/cm²)</u>	<u>Section of Beam Irradiated (cm)</u>	<u>Fraction of SF_6 in "Laser on" Period From Irradiated SF_6</u>
0.2	1.0	0.8
0.4	0.8	0.65
1.5	0.45	0.4

Decay of the excited molecules before they are ionized was neglected in the analysis since spontaneous emission is the only decay mechanism under the collisionless conditions of a molecular beam experiment. The

100 μ s flight time of molecules from the laser beam to the ionization region is certainly much less than the spontaneous emission lifetime (> 1 ms) of highly excited SF_6 .

Now, in the experiment, during the "laser on" period, the photoionization signal e_1 consisted of three parts: Background, b , signal due to SF_6 not irradiated by the laser, $(1-f)s_1$, and signal due to irradiated SF_6 , fs_2 . We have $e_1 = b + (1-f)s_1 + fs_2$. During the "laser off" period, the photoionization signal was $e_2 = b + s_1$. Simple algebra give $e_3 = b + s_2 = e_1/f - e_2(1-f)/f$. Then e_3 and e_2 give respectively the photoionization spectra of the SF_6 pumped and not pumped by the laser. They are plotted in Figs. 2-4 for various cases. The error bars are mainly due to the low count rate in the experiments. Figure 2 shows the SF_6 photoionization spectra for three laser energy fluences with the CO_2 laser tuned to the P(22) line at 942.4 cm^{-1} . Figure 3 shows the spectra for two fluences using the CO_2 P(28) line at 936.8 cm^{-1} .

In Fig. 4 the photoionization spectra of SF_6 without irradiation are given for three different beam nozzle temperatures, 300 K, 500 K and 700 K respectively. The experimental procedure explained in Ref. 12 was used in obtaining these spectra. No substantial relaxation of the vibrational degrees of freedom in the supersonic expansion is expected.¹⁴ Figure 4 also shows theoretical spectra at 500 K and 700 K calculated from the 300 K spectrum, assuming that the excited molecules would have a photoionization spectrum which has the same shape as the

300 K spectrum but is shifted downward by the excitation energy. The experimental spectra however indicate that the downward shift of the spectrum with increasing temperature is rather small. This result suggests that the SF_5^+ ion produced in the photoionization probably keeps most of the excitation energy in the molecule. It makes extraction of more than qualitative information about the level of excitation of SF_6 from Figs. 2-3 very difficult. The smaller change in spectrum from 300 K to 500 K, compared to the greater change from 500 K to 700 K indicates that high frequency SF stretching modes may be more efficient than the low-frequency bending modes in shifting the photoionization spectrum, since the low frequency modes dominate at lower temperatures. However, disregarding such complications, and estimating that some 50-70% of the vibrational energy remains in the ion in the ionization process at 700 K, we can allow ourselves some qualitative statements about the population distribution.

The most striking feature of the photoionization spectra of the laser excited SF_6 is how little they deviate from the spectrum of the unexcited SF_6 . For comparison, we should keep in mind that one CO_2 laser photon of energy corresponds to about 1000 cm^{-1} on the frequency scale. Even at an energy fluence of 1.5 J/cm^2 (see Fig. 2), which is around the dissociation threshold, the spectrum is very similar to the 700 K spectrum of Fig. 4, with somewhat higher average excitation energy. The spectrum does, however, have an excessively long low-frequency tail arising from photoionization of highly excited molecules.. This suggests that most molecules have an average excitation of only about 3 photons, even though

some molecules reach much higher excitation levels. It means that although a large fraction of molecules interact with the laser at the P(22) line, most of them do not absorb enough photons to enter the quasi-continuum for further continuous absorption of photons. Because of the presence of the long high energy tail in the population distribution, the average number of photons absorbed per molecule is higher than 3. This is not in disagreement with the photoacoustic measurements⁶ which show average absorption of around 8 photons per molecule for a 100-200 ns 1.5 J/cm^2 pulse. At these energy fluences, the average energy absorbed by molecules should depend critically on the laser intensity.^{6b,11} The lower peak intensity of our 250 ns pulse is therefore expected to lower the average number of photons absorbed per molecule.

As is evident from Fig. 2, at laser energy fluences much below 1 J/cm^2 , most of the molecules are not excited much beyond 1 photon in energy. This is even more evident from Fig. 3, for a lower laser frequency (P(28) line). However, as the fluence is increased at this frequency, we see an interesting effect: Even though most of the molecules are barely excited at all, a long low frequency tail in the photoionization spectrum appears, indicating that a small fraction of the molecules have been pumped into the quasi-continuum to a fairly high level of excitation, and that this fraction is not too different from the fraction reaching high excitation with the laser tuned to the P(22) lines (see Fig. 2). We have also measured

the spectra when the temperature of the molecules is increased to 500 K, Then there is much less difference between P(28) and P(22) excitation. This shows the effect of hot-band absorption in helping the multiphoton excitation, similar to what we have observed earlier,¹⁵ that the dissociation yield at low laser frequencies can be increased by heating the molecules.

In conclusion, our experiments confirm that in the collisionless multiphoton excitation of SF_6 with low laser intensities, even at the most favorable frequencies, only a small fraction of the molecules will enter the quasi-continuum through near resonant multiphoton absorption, and most of the molecules absorb little energy and remain in the discrete levels, as suggested previously. The observations can be understood by noting that at low laser intensities, only molecules initially occupying certain vibration-rotational states can be easily excited several photons up. For sufficiently high laser intensities, weaker transitions⁵ and power broadening become effective in exciting more molecules into the quasi-continuum. The present experiments on SF_6 is a fairly direct demonstration of the ideas used by Ambartzumian et al.⁹ to explain their experiment on OsO_4 , that at low laser pumping intensities only a small fraction of the molecules ever gets excited into quasi-continuum.

ACKNOWLEDGEMENTS

This work was supported by the Division of Advanced Systems Materials Production, Office of Advanced Isotope Separation, U.S. Department of

Energy under contract No. W-7405-Eng-48. Aa. S. Sudbø also wishes gratefully to acknowledge a fellowship from the Norwegian Research Council for Science and the Humanities.

REFERENCES

1. a) N. Bloembergen and E. Yablonovitch, *Physics Today*, 31 (5), 23 (1978); b) Aa. S. Sudbø, P. A. Schulz, Y. T. Lee and Y. R. Shen, *Proceedings of the First International School on Laser Applications to Atoms, Molecules and Nuclear Physics*, Vilnius, USSR, August 1978; c) C. D. Cantrell, S. M. Freund and J. L. Lyman, in "Laser Handbook", Vol. III (North-Holland, Amsterdam 1978); d) D. J. Krajnovich, H. S. Kwok, Y. T. Lee, P. A. Schulz, Y. R. Shen and Aa. S. Sudbø, in *Annual Reviews of Physical Chemistry*, 30, (1979), eds. B. S. Rabinovich, J. M. Schurr, and H. L. Strauss.
2. J. L. Lyman, *J. Chem. Phys.* 67, 1868 (1977).
3. E. R. Grant, P. A. Schulz, Aa. S. Sudbø, Y. R. Shen, and Y. T. Lee, *Phys. Rev. Lett.* 40, 115 (1978).
4. a) M. Quack, *J. Chem. Phys.* 69, 1282 (1978); b) I. Schek and J. Jortner, "Random Coupling Model for Multiphoton Photofragmentation of Large Molecules", preprint.
5. I. N. Knyazev, V. S. Letokhov, and V. V. Lobko, *Opt. Commun.* 25, 337 (1978).
6. a) V. I. Bagratashvili, I. N. Knyazev, V. S. Letokhov, and V. V. Lobko, *Opt. Commun.* 18, 525 (1976); b) J. G. Black, E. Yablanovitch N. Bloembergen, and S. Mukame, *Phys. Rev. Lett.* 38, 1131 (1977).
7. S. S. Alimpiev, V. N. Bagratashvili, N. V. Karlov, V. S. Letokhov, V. V. Lobko, A. A. Makarov, B. G. Sartakov, and E. M. Khokhlov, *JETP Letters* 25, 547 (1977).
8. A. S. Akhmanov, V. Yu. Baranov, V. D. Pismenny, V. N. Bagratashvili, Yu. R. Kolomiisky, V. S. Letokhov, and E. A. Ryabov, *Opt. Commun.* 23, 357 (1977).

9. R. V. Ambartzumian, G. N. Makarov and A. A. Puretzky, Opt. Commun. 27, 79 (1978).
10. Aa. S. Sudbø, P. A. Schulz, Y. R. Shen and Y. T. Lee, J. Chem. Phys. 69, 2312 (1978).
11. The importance of pulse peak intensity is quite evident from the picosecond pulse experiments of H. S. Kwok, Ph.D. Thesis (Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts, 1978), p. 86.
12. C. Y. Ng, B. H. Mahan and Y. T. Lee, J. Chem. Phys. 65, 1956 (1976).
13. V. H. Dibeler and J. A. Walker, J. Chem. Phys. 44, 4405 (1966).
14. At the nozzle stagnation pressure of about 250 torr that we were using, the relaxation of vibrational degrees of freedom in the supersonic expansion is insignificant.
15. P. A. Schulz, Aa. S. Sudbø, E. R. Grant, Y. R. Shen, and Y. T. Lee, "SF₆ Multiphoton Dissociation by a Molecular Beam Method" (to be published).

FIGURE CAPTIONS

- Fig. 1 Experimental setup: 1) molecular beam; 2) laser beam, 3) UV light beam from monochromator, 4) photoemission nickel metal UV light detector, 5) ion optics.
- Fig. 2 ---- Reference room temperature SF_6 photoionization spectrum.
 ● Spectrum of SF_6 excited by 0.2 J/cm^2 on the P(22) laser line,
 ○ excited by 0.4 J/cm^2 on the P(22) line, and
 ◆ excited by 1.5 J/cm^2 on the P(22) line.
- Fig. 3 ---- Reference room temperature SF_6 photoionization spectrum.
 ○ Spectrum of SF_6 excited by 0.4 J/cm^2 on the P(28) laser line, and
 ◆ excited by 1.5 J/cm^2 on the P(28) line.
- Fig. 4 Photoionization spectra for the reaction $\text{SF}_6 + h\nu \rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$.
 ● Room temperature spectrum.
 — Spectra calculated from the room temperature spectrum for temperatures of 500 K and 700 K.
 ○ 500 K experimental spectrum, normalized to the flat region of the theoretical spectrum.
 + 700 K experimental spectrum, normalized to the flat region of the theoretical spectrum.

XBL 7812-13623

XBL 791-8078

XBL 791-8077

XBL 7812-13615

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720