

## LASER-INDUCED NEGATIVE IONIZATION: THE SF<sub>6</sub> + Ba SURFACE REACTION\*.

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This paper reports on the results about the SF<sub>6</sub> + Ba (surface) reactions as a function of the vibrational excitation of the polyatomic molecule. A thermal, vibrationally excited by a tunable CO<sub>2</sub> laser, SF<sub>6</sub> beam is collided with a Ba surface target under high vacuum conditions. The total negative ion yield is measured as a function of the laser wavelength. Preliminary results show a strong vibrational enhancement of the beam-surface reactions indicating important laser-assisted negative ionization effects. The results are discussed in the light of several possible reaction mechanisms.

KEY WORDS: Beam-Surface Interaction, Vibrational Excitation.

### INTRODUCTION

The importance of vibrational excitation in promoting gas-phase chemical reactions is well known in molecular reaction dynamics.<sup>1</sup> In particular for endoergic reactions this vibrational selectivity has been proved to be a key feature of the so-called late barrier reactions.<sup>2</sup> On the other hand, vibrational excitation is also very important in controlling chemical processes occurring in adsorbed layers.<sup>3</sup> This is a consequence not only of the influence on the lifetime of a molecule on the surface after vibrational excitation, but also of the barrier reduction for chemisorbed molecules in the presence of laser radiation.

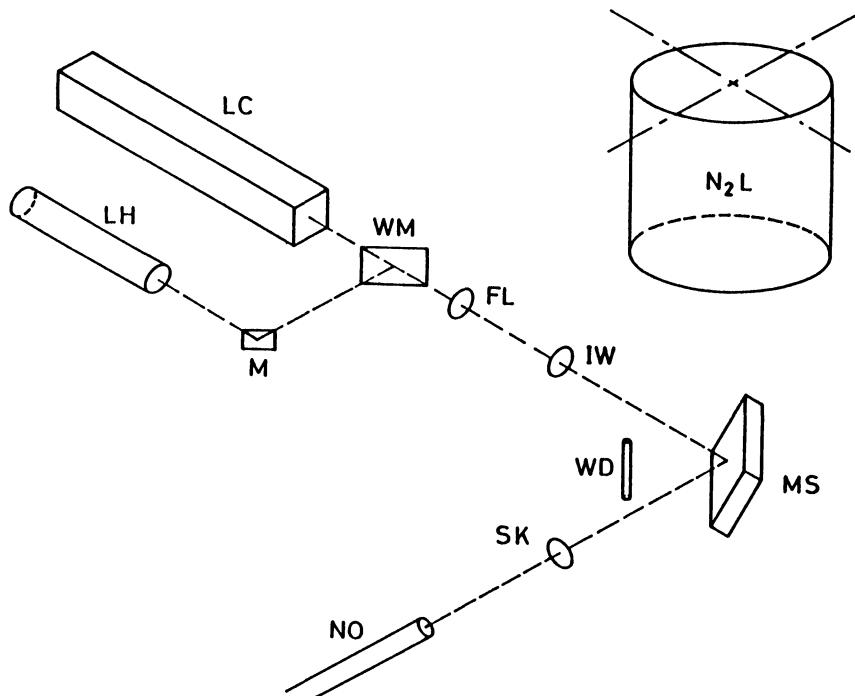
The present paper reports on preliminary results on the formation of negative molecular ions by selective surface ionization under the action of infrared Laser emission.<sup>4</sup> The study is based on the well known fact that the yield of negative ions in the interaction of molecules with heated surfaces may be as high as 99% for some

hexafluorides.<sup>5</sup> In addition the choice of SF<sub>6</sub> molecule is also very convenient because several lines of a CO<sub>2</sub> laser can be used to pump rovibrationally its ν<sub>3</sub> band.<sup>6</sup> Thus the influence of vibrational excitation on the laser-assisted beam-surface ionization can be studied providing insight into the dynamics of the underlying physi and chemisorption processes.

## EXPERIMENTAL

A schematic view of the laser-beam apparatus is displayed in Figure 1. Briefly an effusive SF<sub>6</sub> beam impinges on a polycrystalline Ba surface. A tunable CO<sub>2</sub> laser is used to excite the thermal SF<sub>6</sub> beam as well as to heat the Ba surface. This is accomplished by focusing the laser on the surface collimated area at which the molecular beam collides. This procedure ensures not only a cleaner surface, but also a constant surface temperature while the laser wavelength is slowly tuned.

In front of the surface there is an ion collector to monitor the ion yield as the wavelength is changed. A typical run consists of measuring the ion yield by using a continuous SF<sub>6</sub> beam excited by a modulated CO<sub>2</sub> laser beam. For a given wavelength, the net signal consists of negative ion current with both the laser and



**Figure 1** Schematic view of the experimental set up. LC, CO<sub>2</sub>, Laser, LH, Helium-Neon Laser. M, mirror. WM, Mixer mirror. FL, focal len. IW, infrared wall. MS, metal surface. WD, Ion collector. NO, nozzle oven. SK, Skimmer.

beam on minus the background signal with the beam on and laser off. The signal properly amplified and filtered by a lock-in amplifier is then measured as a function of the CO<sub>2</sub> laser wavelength.

Table I summarises the most relevant experimental conditions of the present work.

**Table 1** Experimental Conditions

<b>Laser system</b>	
Wavelength range/μm	9–11
Power/W	4.8
Frequency Modulation/Hz	30.1
Duty Cycle/%	50
<b>Vacuum</b>	
pressure/torr	1–3.10 <sup>-6</sup>
Barium Temperature/K	1300–1600
Beam Density/atom cm <sup>-3</sup>	10 <sup>10</sup>
<b>Electronics</b>	
Bias Voltage/V	36
Amplification factor/VA <sup>-1</sup>	10 <sup>11</sup>

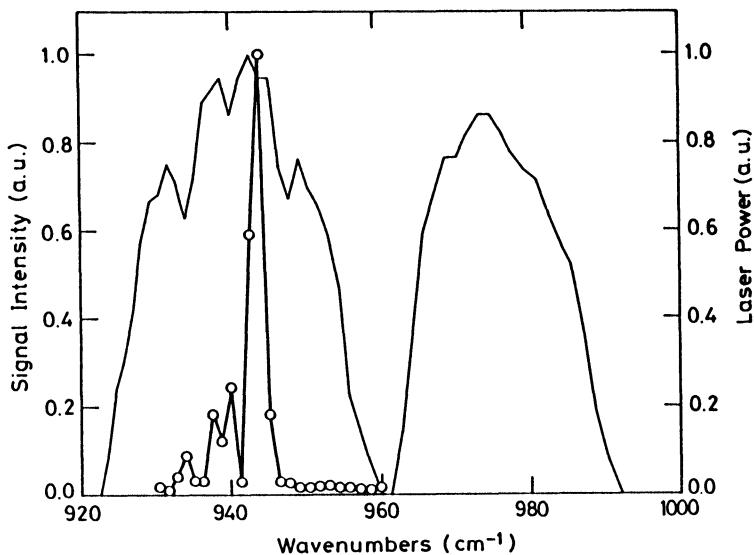
## RESULTS AND DISCUSSION

### *Laser-induced negative ionization*

Figure 2 shows a typical laser-induced negative ionization spectrum taken under the experimental conditions of Table I. Table II lists the ion current intensities observed in a typical run. It is interesting to point out the lack of positive ion current even with both the laser and beam on. In addition the good signal to noise ratio e.g. laser on beam on/beam off is noticeable and rules out the possible contribution of the thermoionic emission to the observed signal. The thin solid line represents the CO<sub>2</sub> laser power as a function of the wavelength. The heavy solid line through the open circles corresponds to the measured negative ion current at the same experimental conditions. One of the most significant aspects of the present results is the non-thermal character of the observed phenomenon. Notice, for example, the absence of signal at  $\nu = 980\text{ cm}^{-1}$  in spite of the fact that the laser power, and likely the surface temperature, is about the same as that for  $\nu = 945\text{ cm}^{-1}$ . The clear vibrational enhancement of the ion yield, underlying this energy (laser wavelength) selectivity, is evident.

**Table 2** Typical Ion Current Intensities

	Positive Ion Current LASER		Negative Ion Current LASER	
	ON	OFF	ON	OFF
<b>ON</b>	0 pA	0 pA	84 pA	0 pA
<b>BEAM</b>				
<b>OFF</b>	0 pA	0 pA	1.5 pA	0 pA



**Figure 2** Negative ion signal (circles) and laser power as a function of laser wavenumber.—Laser power (ordinate scale in arbitrary unit on the right). Negative ion signal in arbitrary units. The signal corresponds to the total negative ion signal collected as the SF<sub>6</sub> beam impinges on the Ba surface. Notice the clear selectivity of the experimental data. i.e. No signal is observed beyond  $\nu > 960\text{ cm}^{-1}$ . Laser linearly polarized at 90 degrees with respect to the surface normal.

### Possible reaction mechanisms

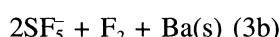
Unfortunately the negative ion yield spectrum was taken without mass selection. Therefore the total negative ion signal may well be due to several possible products: the fast SF<sub>6</sub><sup>-</sup> and the slow SF<sub>5</sub><sup>-</sup>. These two ions can be produced by the following processes

(i) fast, non-reactive negative ionization

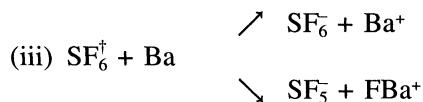
1. SF<sub>6</sub> + hν (IR CO<sub>2</sub> laser) → SF<sub>6</sub><sup>+</sup>
2. SF<sub>6</sub><sup>+</sup> + Ba(s) → SF<sub>6</sub><sup>+</sup> . . . Ba(s) → SF<sub>6</sub><sup>-</sup> + Ba(s)  
(Physisorption)

(ii) slow, reactive negative ionization

1. SF<sub>6</sub> + hν (IR CO<sub>2</sub> laser) → SF<sub>6</sub><sup>+</sup>
2. SF<sub>6</sub><sup>+</sup> + Ba(s) → SF<sub>6</sub><sup>+</sup> . . . Ba(s)  
(Chemisorption)



In principle, from a theoretical point of view, one could also consider another possibility: that is the negative gas-phase ionization.



induced by fast laser desorption of the Ba metal and multiphoton excitation of the polyatomic molecule. Such multiphoton excitation process is necessary since the ground state reactions represented by *iii* are endoergic or require a translational energy threshold<sup>7</sup> higher than the total kinetic energy available in the present experiment ( $E_T = 0.1$  eV). The fact that we observe no positive signal when we reverse the collector bias (e.g. to collect positive ions) in addition to the lack of multiphoton processes (see below) rules out the mechanism outlined by equation (iii).

In view of the lack of the mass selection, as pointed out earlier, we are unable to distinguish which reaction pathway e.g. **i** or **ii** is responsible for the observed laser-assisted negative ionization. We believe we may have both of them.

#### *Comparison with other SF<sub>6</sub> spectra*

Another crucial aspect of the present work is to know whether multiphoton or single photon excitation is responsible for the beam-surface ionization process.

Figure 3 compares the present laser-assisted negative ion formation with: (a) the SF<sub>6</sub> linear absorption cross-section (single-photon gas-phase absorption) from Ref. 8 and (b) the SF<sub>6</sub> multiphoton dissociation rate as a function of the laser wavelength, from Ref. 9. It is interesting to point out the red shift of the present spectrum with respect to the linear uniphoton, gas-phase absorption cross-section of the SF<sub>6</sub>.

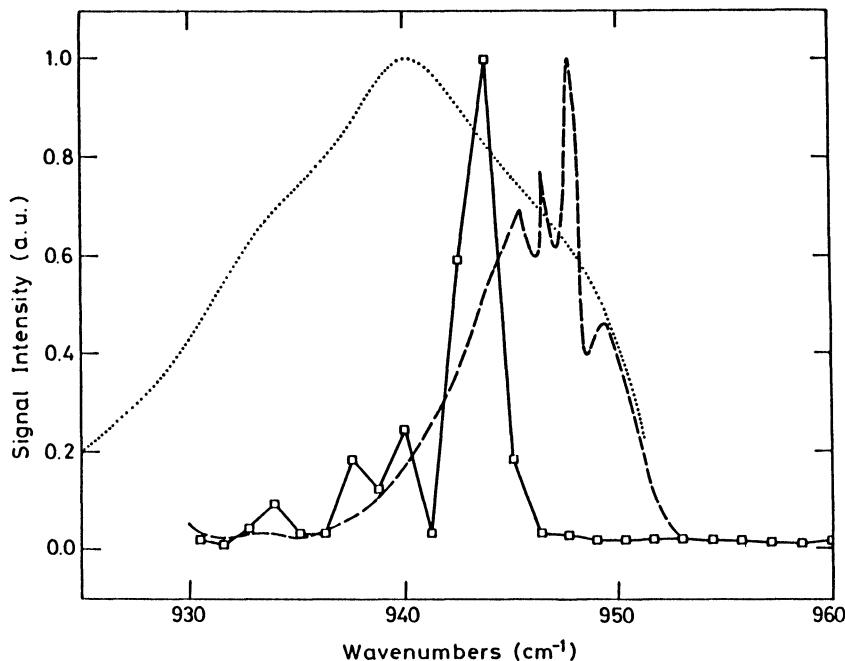
In spite of the red-shift of the observed spectrum with respect to the single-photon absorption data, it is interesting to point out the close similarity between these two spectral shapes. On the other hand, the significant difference of the present data with respect to the multiphoton absorption spectrum rules out the role of the multiphoton processes. It appears that the observed laser-assisted negative ionization is a single-photon process which red-shift might be due to the softening of the intermolecular potential of the adsorbed SF<sub>6</sub>.

Work is now in progress to unravel the molecular mechanism of this laser-assisted surface ionization by means of time-of-flight analysis of the reaction products.

#### *References*

1. R. D. Levine and R. B. Bernstein. "Molecular Reaction Dynamics and Chemical Reactivity". Oxford University Press. Oxford 1987.
2. A. González Ureña. *Adv. Chem. Phys.*, **66**, 213 (1987)
3. See for example the Book of Abstracts of the European Conference on Gas-surface Dynamics. August. Graz, Austria 1992.
4. J. Castaño Aspas and A. González Ureña. Contribution D. 20 in Ref. 3.
5. P. F. Dittner, S. Datz. *J. Chem. Phys.*, **68**, 2451 (1978)

6. F. Brumer and D. Droch. *J. Chem. Phys.*, **68**, 4936 (1978)
7. See for example U. Ross, H. J. Meyer & Th. Schuze. *Chem. Phys. Letters.*, **84**, 359 (1984)
8. A. V. Nowak and J. L. Lyman. *J. Quant. Spectrosc. Radiat. Transfer*, **15**, 945 (1975).
9. R. V. Ambartsumian, V. S. Letokhov. In *Chemical and Biochemical Applications of Lasers*. Volume 3 (C. B. Moore, ed.) Academic, New York (1977). Chapter 2.



**Figure 3** Negative ion signal as a function of laser wavenumber. Present experimental results as displayed in Figure 2. Dashed line is the linear, single-photon, absorption cross-section of the SF<sub>6</sub> from Reference 8. Dotted line stands for the multiphoton dissociation rate taken from Reference 9. Notice the red shift and similarity of the present observed results with respect to the linear absorption spectrum