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Spectral and Temperature Dependence of Laser Induced Dissociative Attachment in SF₆

R. BARBE, J.-P. ASTRUC, A. LAGREZE and J.-P. SCHERMANN

*Laboratoire de Physique des Lasers, Associé au C.N.R.S. n°282 Centre
Scientifique et Polytechnique, Université Paris-Nord - 93430 - Villetaneuse,
France*

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We consider the influence of resonant laser excitation upon the dissociative reaction between SF₆ molecules and very low energy electrons. Experimentally, the use of valence electrons of atoms in Rydberg states ensures a well-defined energy resolution of the scattering electrons in the crossed beam apparatus. A spectroscopic model of the infrared absorption of CO₂ laser radiation by SF₆ gives a fair determination of the energy levels and vibrational transitions involved in the dissociative process. This reaction between highly excited atoms and a molecule is interpreted as a three step process: attachment of a quasi-free electron, followed by the interaction between the atomic ionic core and the negative molecular ion leading to a partial stabilization and, finally, the competition between the dissociating and the auto-detachment channels.

INTRODUCTION

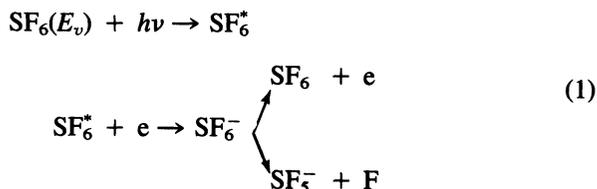
The multiple photon dissociation (MPD) of SF₆ into neutral components occurs in two stages,¹ one involving a resonant excitation of the first few discrete vibrational states of the ν_3 ladder, the other leading to dissociation by absorption of a large number of photons within the vibrational quasi-continuum.

An alternative approach to isotopically selective dissociation of SF₆ has been proposed and studied by several authors.²⁻⁴ In this approach, one takes advantage of a well-known property of SF₆: it attaches low energy electrons and, according to its vibrational energy, the negative ion produced

is either SF_6^- or SF_5^- . Thus, the resonant vibrational excitation can strongly modify the branching ratio between the non-dissociative and dissociative channels [Figure 1]. The large amount of nonresonant laser energy which is required in the second step of the MPD dissociation into neutral components is replaced by chemical energy, i.e. the electron affinity of the SF_5 product.

A modeling of the above processes requires a good knowledge of the collision conditions (for instance, single collision conditions), of the SF_6 internal energy and the electron energy distribution. Reciprocally, such a model provides information about the dynamics of low energy electron- SF_6 scattering (attachment, autodetachment and dissociation lifetimes . . .) and parameters of laser excitation.

We report here the spectral and temperature dependence of the following reactions:



where $\text{SF}_6(E_v)$ corresponds to SF_6 molecules with an internal energy E_v controlled by means of temperature and SF_6^* to laser excited molecules. In order to obtain a knowledge of the electron energy distribution as accurately as possible, we use valence electrons of atoms in Rydberg states. Experimentally, this way of producing sub-thermal electrons is somewhat similar to the use of a photoionisation source of quasi monoenergetic electrons.⁵ In comparison with more conventional techniques⁶ such as RPD spectrometers or swarm experiments in which the electron energy distributions are approximately 100 meV wide with long energy tails, the use of electrons bound to highly excited atoms sets an upper limit to the maximum kinetic energy of the electrons attaching to SF_6 . As far as attachment alone is concerned, it has been shown by Matsuzawa⁷ that these bound electrons behave as if they were free, with momentum distributions governed by the quantum states of the highly excited atoms. The fate of the negative ion created by this charge exchange may, however, be influenced by the presence of the remaining ionic core, leading to a stabilization process.⁸

For a wide range of temperature and, thus, of internal energy of the

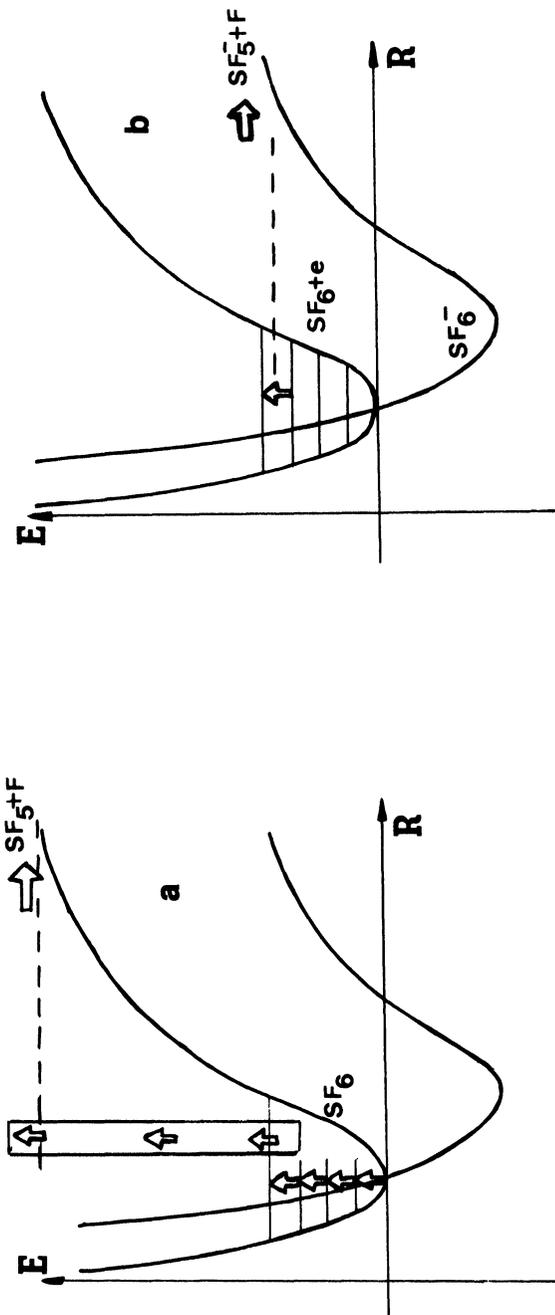


FIGURE 1 Potential energy curves of SF_6 and SF_6^- in a diatomic representation. *1a*: The multiple photon dissociation of SF_6 into neutral components occurs in two stages, the first one involving a resonant vibrational ladder and the second, absorption in a quasi-continuum. The first step is isotopically selective and the second provides most of the energy leading to dissociation. *1b*: When a SF_6 molecule with internal energy lower than the threshold for dissociation attaches a zero energy electron, the negative ion produced is SF_6^- . Above this threshold, the negative ion produced is the more reactive SF_5^- . A single photon absorption can strongly modify the ionic out-come.

parent SF₆ molecules, we measured the influence of resonant laser excitation upon the reaction (1) for all CO₂ laser lines corresponding to the absorption of the isotopic molecule ³²SF₆. Our results agree reasonably well with those of Chen and Chantry³ in respect of the spectral dependence of the process. Their experiment and interpretation concerning the laser excitation and energy threshold were in disagreement with previous measurements of the activation energy of the reaction. We attribute this disagreement to the problem of electron energy distributions in RPD techniques.

By analyzing our results with a spectroscopic model of CO₂ laser absorption by SF₆, derived from the model of Nowack and Lyman,⁹ we interpret the red shift of the dissociative channel with respect to the low temperature small signal absorption curves and we show that single photon excitation is responsible for the laser induced process. From our data, we confirm the accepted value of energy threshold of the reaction (1) and show that, following the suggestion of Nowack and Lyman, one must add to their model the variation of the rotational constant as a function of vibrational energy. We also demonstrate that one has to take into account, for high excitation levels, the competition between the two exit channels of reaction (1), i.e., dissociative attachment and autodetachment.

APPARATUS

A schematic diagram of the experimental arrangement is shown in Figure 2. This cross beam experiment, which satisfies the single collision condition, will be described in more detail in a forthcoming paper.¹⁰ A beam of SF₆ molecules, emanating from a platinum tube (1 mm i.d. 10 cm long) with variable temperature from 300°K to 1000°K crosses a beam of argon atoms excited to Rydberg states. These highly excited atoms which act as a source of low energy electrons, are produced by electron bombardment. Their time of flight between their creation and the collision region is approximately 200 μs. The competition between the cross-section for creation of these atoms in the state of a principal quantum number n (low orbital quantum number l) which varies as n^{-3} , and the radiative lifetimes which vary as n^α where $4 < \alpha < 5$ (for large values of l after redistribution among l by collisions undergone after creation) results in an energy distribution of the electrons between 10 and 40 meV ($18 < n < 35$) as confirmed by field ionization measurements.¹⁰

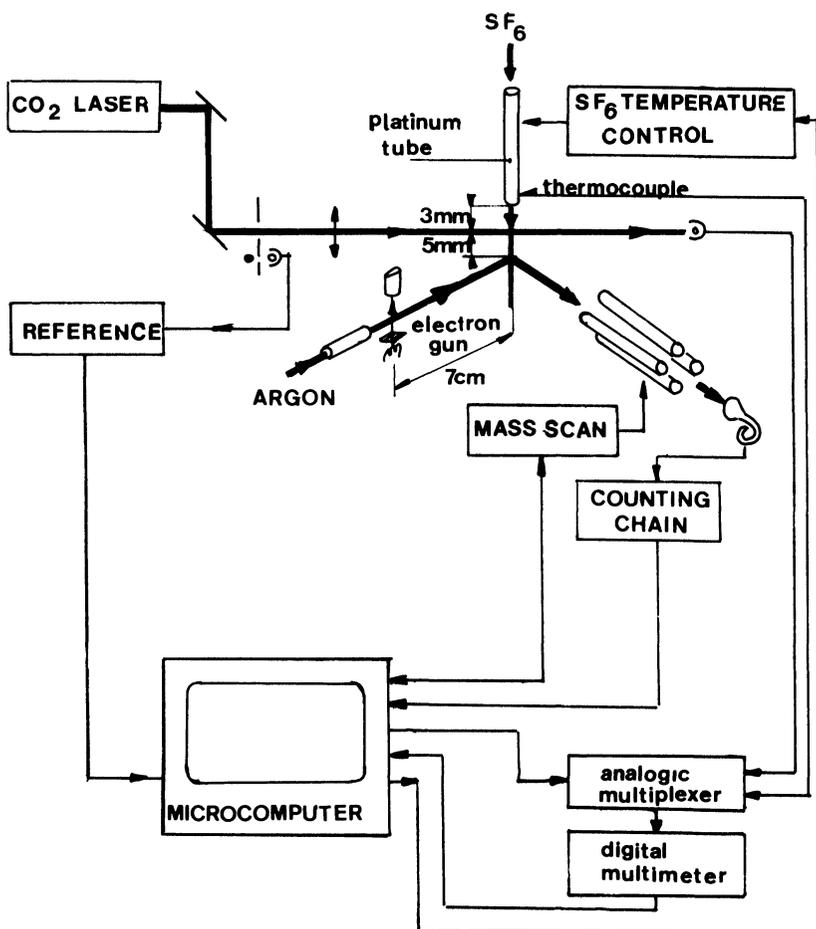


FIGURE 2 Experimental set-up. The SF₆ beam with computer controlled temperature (varying between 300°K and 1000°K), is excited by the CO₂ laser beam. The chopping reference drives the up-counting and down-counting in the micro-computer. The laser excited SF₆ beam crosses the high Rydberg argon atomic beam and the ionic products are mass-analyzed by a quadrupole-spectrometer.

A CW 4W CO₂ laser, which is grating tuned, is focused at the exit of the platinum tube and a fraction of the SF₆⁺ beam is excited in the .8 mm diameter laser waist. In order to monitor the number of SF₅⁻ ions (detected by a quadrupole mass analyzer) produced, due to laser vibrational excitation, ON - OFF synchronous detection is done by a microcomputer

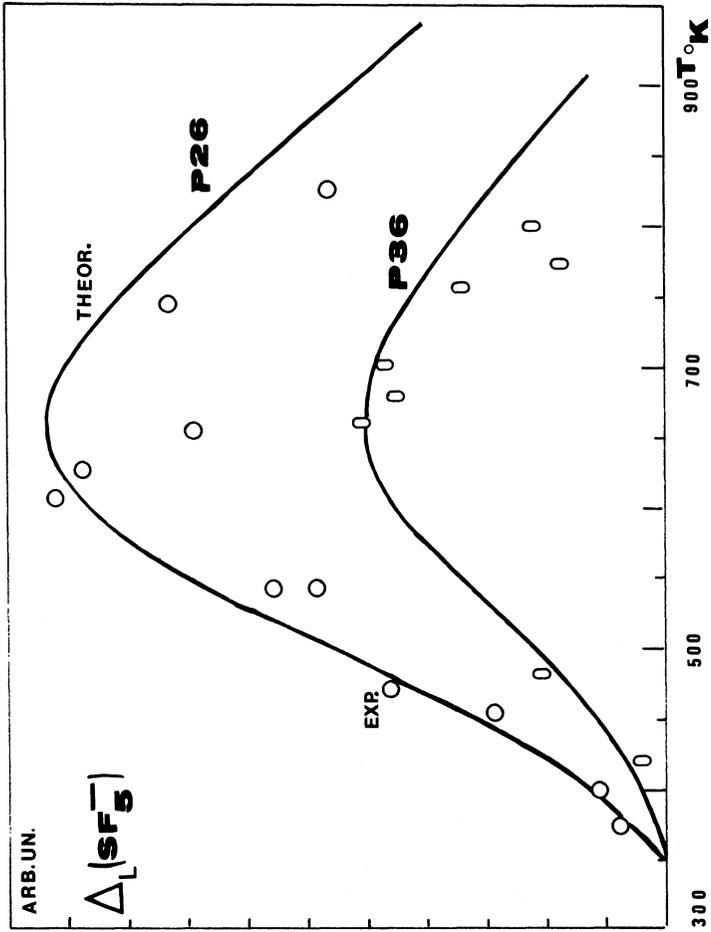


FIGURE 3 The laser induced signal $\Delta_L(\text{SF}_5^-)$ is the modification of the number of SF_5^- ions due to resonant laser absorption. This signal is plotted as a function of the SF_6 beam temperature for two characteristic laser lines. The dotted lines are experimental and full lines correspond to the spectroscopic model.

clocked by the laser chopper. Typical $^{32}\text{SF}_5^-$ ion signals due to the laser are 15 counts/sec. with an averaging time of 60 sec. The weakness of these signals, due to the crossing beam intensities, did not allow us to observe $^{34}\text{SF}_5^-$ ion signals, restricting our study to the most abundant isotope $^{32}\text{SF}_6$ (95%).

Experimental results

For several CO₂ laser lines corresponding to the absorption band of $^{32}\text{SF}_6$, the relative enhancement of the $\text{SF}_6^- \rightarrow \text{SF}_5^- + \text{F}$ dissociative channel, as a function of the SF₆ parent molecule temperature, was measured (Figure 3). The qualitative behavior is the same for the different laser lines: the laser induced SF₅⁻ signal rises around 400°K, culminates near 600°K and decreases at higher temperatures.

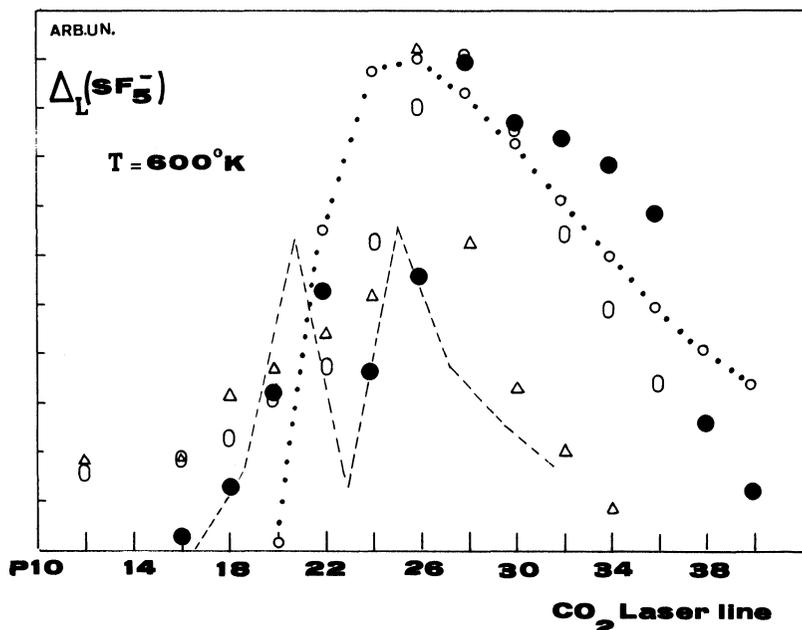


FIGURE 4 The laser induced signal is plotted as a function of the CO₂ laser lines for several experiments ○ Chen and Chantry (Ref. 3) Δ Avrillier and Schermann (Ref. 2) and ● this experiment. The dotted line corresponds to the spectroscopic model with a new value of the anharmonic constants and variation of the rotation constant. The broken line corresponds to the original model of Ref. 9.

At a temperature of 600°K at which the laser induced SF_5^- signal is maximum, the dependence of this signal upon the CO_2 laser lines is shown in Figure 4. This measurement agrees reasonably well with that of Chen and Chantry³ obtained with an RPD technique and that of Avriillier and Schermann² obtained by an optogalvanic detection in a SF_6 discharge.

The power dependence of the laser induced signal is shown in Figure 5. The maximum power available corresponds to a power broadening of about 70 MHz as compared with the 30 MHz Doppler linewidth. In the vibrational excitation region that we consider where $E_v \sim 3500 \text{ cm}^{-1}$, there are approximately 10^2 vibrational levels per cm^{-1} and, thus, one level every 300 MHz which may absorb. This interval is larger than the laser broadening.

The interaction time of the SF_6 molecules inside the laser beam waist is 2 μs . With a CO_2 laser photon absorption cross-section of 10^{-18} cm^2 ,

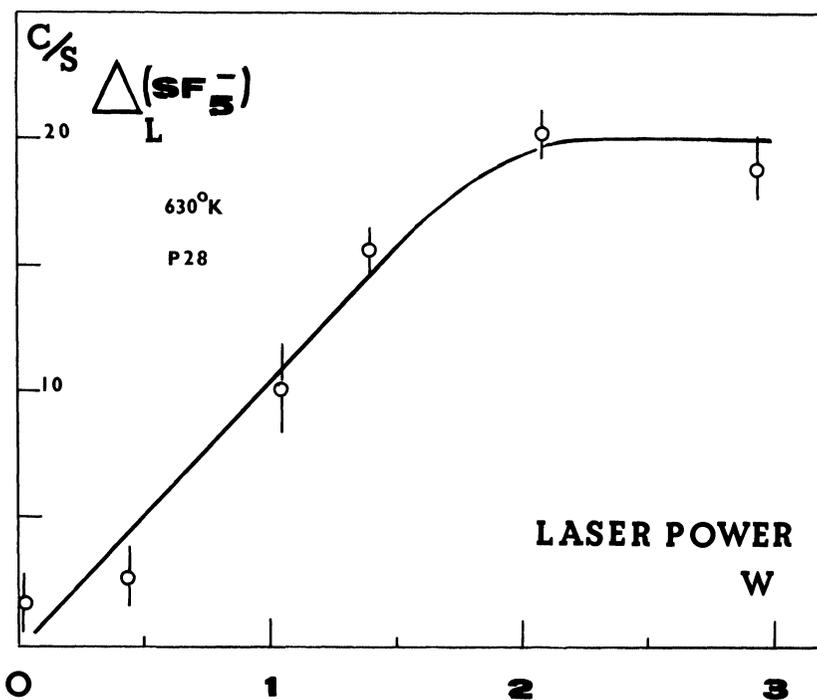


FIGURE 5 The laser induced signal is plotted, as a function of the CO_2 laser power for SF_6 temperature of 630°K and the P28 CO_2 laser line for which this signal is maximum.

saturation is obtained for a few kW/cm². We thus interpret the power dependence as a linear variation followed by saturation when the probability of excitation of a SF₆ molecule reaches unity.

Spectroscopic model

The modeling of the first discrete multiple photon stage of excitation in MPD of SF₆ has provided a strong impetus for the determination of the infrared spectrum of this molecule. Till now, a precise interpretation of the very high resolution spectrum has only been made for the ν_3 fundamental transition,¹¹ together with a Doppler limited analysis¹² of the $\nu_3 \rightarrow 2\nu_3$ second harmonic and a determination¹³ of the ν_3 vibrational ladder. Very little information is available about the rovibrational spectrum of the other modes, even at low resolution. We have thus used for our spectral analysis the model of Nowack and Lyman⁹ with some modification of the anharmonicity constant, recently determined,¹³ and the energy dependence of the rotational constant which was necessary to introduce in order to fit our data to the initial values of Ref. 9. We shall give here only a brief account of this model referring to the original paper.

The vibrational states of SF₆ are defined by a set of vibrational quantum numbers $[v_i]$ corresponding to the 6 normal modes. The only anharmonicity constant which has been precisely measured corresponds to the ν_3 mode and we adopt the empirical Nowack and Lyman proposal which states that, for each mode, the harmonic shift of a vibrational overtone is proportional to the frequency ν_i of the fundamental. Ignoring rotation energy, the frequency of a transition involving a ν_3 photon, originating from a state $[v_i]$ is then given by:

$$\nu_o[v_i] = \nu_o(0) + A \sum_i \nu_i v_i \quad (2)$$

where $\nu_o(0)$ is the frequency of the ν_3 transition originating from the ground state. This unique proportionality constant A is related to the anharmonicity constant X_{33} by the relation $X_{33} = \frac{1}{2}A\nu_3$. We take for X_{33} the experimental value of Ref. 13 $X_{33} = -1.74 \text{ cm}^{-1}$.

For vibrational energies E_v of states $[v_i]$ ranging from 0 to 1650 cm⁻¹, we use direct count of these levels. Above this value, the density of states is high enough to consider the vibrational level distribution as quasi continuous. As in Ref. 9, we define as "levels" those which consist of all

states with vibrational energy in the range $E_v \pm 10 \text{ cm}^{-1}$. These levels are related to a set of mean values of the vibrational quantum numbers $[\bar{v}_i]$. The fraction of molecules at energy E_v which have v_i quanta of mode v_i is:

$$F(v_i, E_v) = \frac{g(E_v - v_i v_i, S = 15 - d_i)}{g(E_v, S = 15)} \times D \quad (3)$$

where D is a degeneracy factor equal to 1 for the non-degenerate mode v_1 , and is equal to $v_i + 1$ for the doubly degenerate mode v_2 and $(v_i + 1)(v_i + 2)/2$ for the other triply degenerate modes and d_i the degeneracy of mode v_i .

The densities $g(E_v)$ are computed by means of the Whitten and Rabinovitch expression.¹⁴ For each value of E_v there correspond possible integer values of v_i from 0 to $x = \text{integer}(E/v_i)$ and the mean value of v_i is then

$$\bar{v}_i = \sum_{v_i=0}^x F(v_i, E_v) v_i \quad (4)$$

In Ref. 9, it was assumed that if B' and B'' are respectively the rotational constant of the upper and lower states involved in a laser transition, one can neglect the difference $B' - B'' = \Delta B$ as compared to B' and B'' . We found it necessary to take into account the linear variation¹⁵ of the rotational constant B and the Coriolis coupling ζ as functions of the vibrational energy E_v , thus expressing empirically, the effective rotational constant as:

$$B(E_v) = B_e - \alpha E_v \text{ with } \alpha = \alpha_0 + \beta E_v \quad (5)$$

For each level characterized by a vibrational energy E_v and quantum numbers $[v_i, J]$ or $[\bar{v}_i, J]$, there correspond three absorption lines P , Q and R which may coincide with the CO_2 laser lines of frequency ν_L (in cm^{-1}) for certain values of J , solutions of the following numerical equations

$$P \text{ branch } \nu_L = \nu_o[\nu_i] - [-0.0538 + 6.2610^{-4} E_v - 0.406\alpha] J - \alpha J^2$$

$$Q \text{ branch } \nu_L = \nu_o[\nu_i] + \alpha J(J + 1)$$

$$R \text{ branch } \nu_L = \nu_o[\nu_i] + [0.0538 - 6.2610^{-4} E_v - 1.594\alpha] J - \alpha J^2$$

For a given temperature of SF₆, taking into account the vibrational and rotational partition functions, these values of J , corresponding to spectral coincidences, determine, within a constant factor, the absorption coefficient $dk(\nu_L, E_v)$ of the different CO₂ laser lines (of frequency ν_L), by each "vibrational level" (of energy E_v). In this band contour model, our only adjustable constants are the linear α and quadratic β coefficients of the rotational constant B .

Collision model

We use, as a source of thermal electrons, a beam of argon atoms in Rydberg states which ensure a well controlled energy distribution of these electrons. The collision between the highly excited atoms and the SF₆ molecules is a three step process. First, the quasi free electron, with negligible kinetic energy, as compared to the internal energy E_v of the colliding SF₆ molecule, attaches with a cross-section independent of E_v .¹⁶ The negative ion thus produced possesses an internal energy $E_v + EA$ where EA is the adiabatic electron affinity of SF₆. This ionic core of the excited argon atom suffers Coulomb attraction from the SF₆⁻ ion and, in a second step, both ions exchange energy, i.e., part of the internal energy of the SF₆⁻ ion can be transferred as kinetic energy to the ionic core. This corresponds to the stabilization process of Zembekov⁸ where, at the end of the collision, the negative ion is left with an internal energy $E_v + EA - \Delta E$. Depending on this energy $E_{v'}$, in a third step, the negative ion can autodetach with an autoionization rate $\tau_a^{-1}[E_{v'}]$, be stabilized (an "infinite" lifetime vs autodetachment) or dissociate with a rate $\tau_d^{-1}[E_{v'}]$ (Figure 6).

The dependence of τ_a , τ_d versus the internal energy $E_{v'}$ of the negative ion can be estimated by means of RRKM statistical theories^{17,18} or by the inverse Laplace transform of the measured values of negative ion production as a function of temperature.^{10,19,20} The autodetachment lifetime τ_a slowly decreases for $E_{v'}$ between 4000 and 8000 cm⁻¹ with a mean value cc. 10 μ s, then drops very small values for $E_{v'}$ above 8000 cm⁻¹. The dissociation lifetime τ_d decreases strongly near the threshold energy E_d of

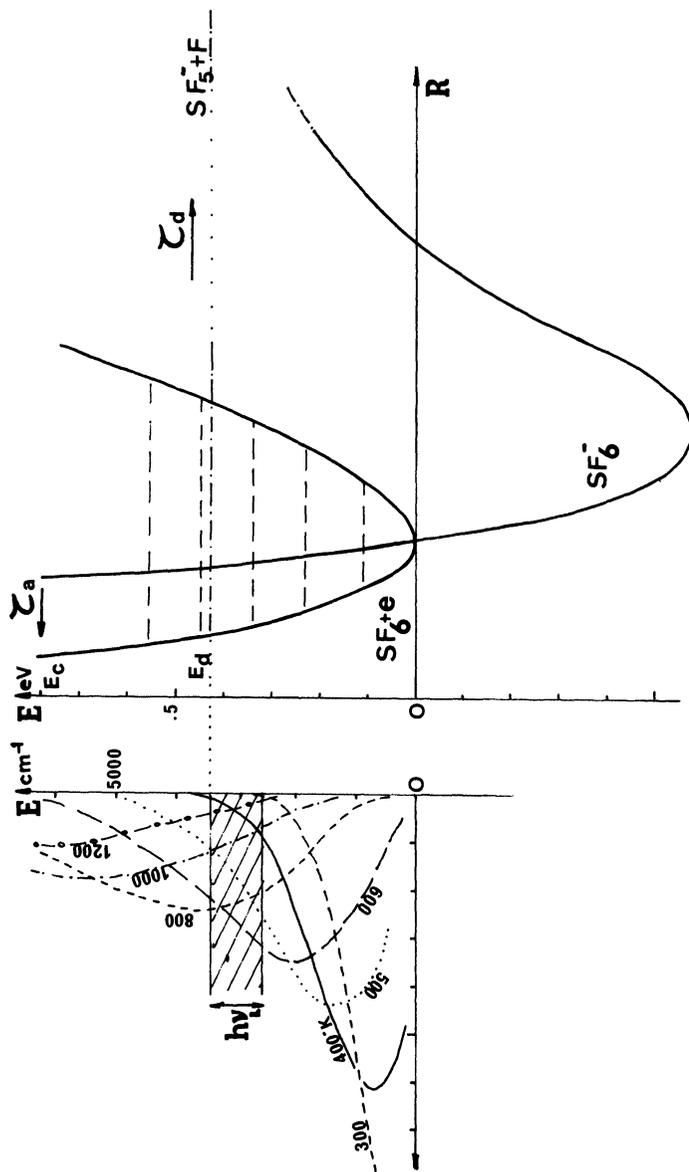


FIGURE 6 The relative vibrational densities are plotted as a function of the vibrational energy, for different temperatures. The shaded area corresponds to the fraction of molecules with internal energy between $E_d - hv_L$ and E_d , where E_d is the dissociation energy and hv_L the CO_2 laser photon energy.

the dissociative reaction $SF_6^- \rightarrow SF_5^- + F$, then slowly between 5000 and 8000 cm^{-1} around a value of 30 μs .

After the absorption by an SF₆ molecule with energy E_v of a laser photon of frequency ν_L , a negative SF₆⁻ ion is produced with an internal energy $E_{v'} = E_v + h\nu_L = E_v + EA - \Delta E + h\nu_L$. During its time of flight τ_p between its creation and its detection this SF₆⁻ ion can autodetach or dissociate into SF₅⁻. For each "vibrational level", the variation of the number of detected SF₅⁻ ions due to the laser is given by:

$$dN(SF_5^-)_{laser} = C \frac{P}{S} dk(\nu_L, E_v) \left\{ \left[1 - \exp - \left(\frac{\tau_p}{\tau_a(E_{v'})} + \frac{\tau_p}{\tau_d(E_{v'})} \right) \right] \frac{\tau_a(E_{v'})}{\tau_a(E_{v'}) + \tau_d(E_{v'})} - \left[1 - \exp - \left(\frac{\tau_p}{\tau_a(E_{v'})} + \frac{\tau_p}{\tau_d(E_{v'})} \right) \right] \frac{\tau_a(E_{v'})}{\tau_a(E_{v'}) + \tau_d(E_{v'})} \right\}$$

where P is the laser power, S the laser beam area and C the proportionality constant. $(P/Sh\nu_L) dk(\nu_L, E_v)$ is the number of molecules, in the "vibrational level" E_v , excited per second and per unit of volume.

The dissociative channel is open to a SF₆⁻ ion ($E_{v'} > E_d$) when its parent molecule internal energy E_v is above the energy threshold $E_{th} = E_d + \Delta E - h\nu_L$. Thus, the total SF₅⁻ ions due to the laser absorption is

$$N(SF_5^-)_{laser} = \int_{E_{th}}^{\infty} dN(SF_5^-)_{laser}$$

If we assume that τ_a and τ_d are constant above the energy threshold $E_{v'} \geq E_d + EA$ and that τ_d is infinite for $E_{v'} < E_d + EA$ then the laser has no effect upon molecules with energy $E_v \geq E_d + \Delta E$ since $\tau(E_{v'}) = \tau(E_{v'})$. We obtain a simple expression:

$$\begin{aligned}
 N(\text{SF}_5^-) \text{ laser} &= \int_{E_{ih}}^{E_d + \Delta E} C \frac{P}{S} dk(\nu_L, E_\nu) \\
 &\cdot \left\{ \left[1 - \exp - \left(\frac{\tau_p}{\tau_a} + \frac{\tau_p}{\tau_d} \right) \right] \frac{\tau_a}{\tau_a + \tau_d} \right\} \\
 N(\text{SF}_5^-) \text{ laser} &= \frac{C'P}{S} \int_{E_{ih}}^{E_d + \Delta E} dk(\nu_L, E_\nu)
 \end{aligned}$$

The results corresponding to this model are shown in Figure 7 (broken line $E_c = 0$).

In order to take into account the decrease of the branching ratio between dissociation and autodetachment observed in experiments with SF_5^- and SF_6^- ,¹⁰ the preceding model can be improved by assuming that the autodetachment lifetime $\tau_a(E_{\nu'})$ is constant up to $E_{\nu'} = EA + E_c$, and for $E_{\nu'} \geq E_c + EA$. ($\tau_a(E_{\nu'}) = 0$.) This critical value E_c is to be determined. With this assumption, we obtain

$$\begin{aligned}
 N(\text{SF}_5^-) \text{ laser} &= \int_{E_{ih}}^{E_d + \Delta E} C \frac{P}{S} dk(\nu_L, E_\nu) \\
 &\times \left[1 - \exp - \left(\frac{\tau_p}{\tau_a(E_{\nu'})} + \frac{\tau_p}{\tau_d(E_{\nu'})} \right) \right] \frac{\tau_a(E_{\nu'})}{\tau_a(E_{\nu'}) + \tau_d(E_{\nu'})} \\
 &- \int_{E_c + \Delta E - h\nu_L}^{E_c + \Delta E} C \frac{P}{S} dk(\nu_L, E_\nu) \\
 &\left[1 - \exp - \left(\frac{\tau_p}{\tau_a(E_{\nu'})} + \frac{\tau_p}{\tau_d(E_{\nu'})} \right) \right] \frac{\tau_a(E_{\nu'})}{\tau_a(E_{\nu'}) + \tau_d(E_{\nu'})}
 \end{aligned}$$

The full line on Figure 7 corresponds to the best fit with $E_c = 8500 \text{ cm}^{-1}$.

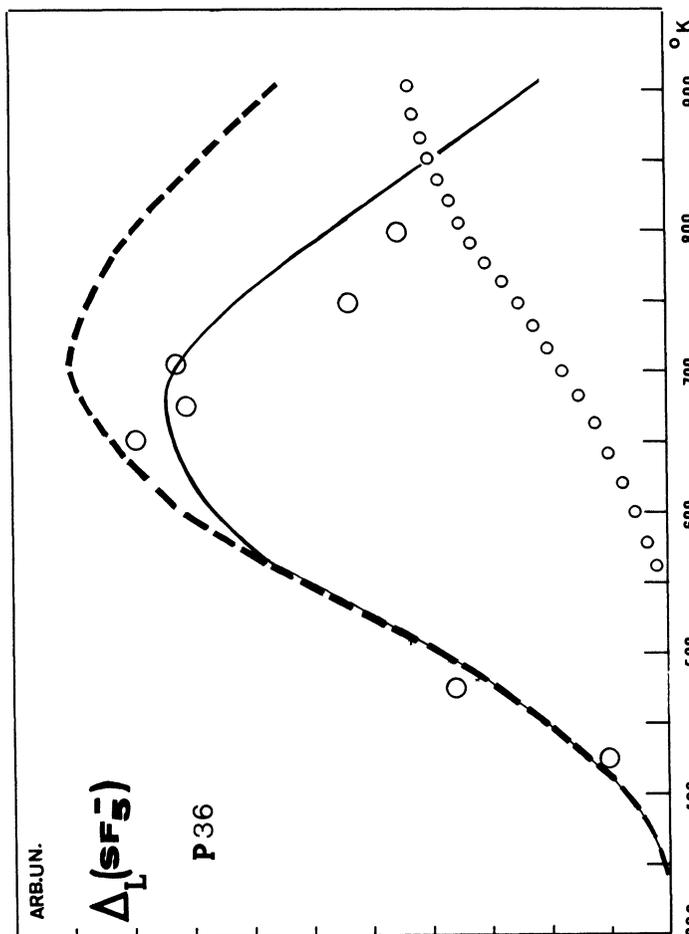
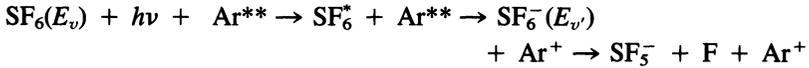


FIGURE 7 The laser induced signal is plotted as a function of the SF₆ temperature for the P36 CO₂ laser line. The circles are the experimental values. The broken line corresponds to the spectroscopic model ignoring the autodetachment channel. The dotted line represents the number of SF₆⁻ ions which autodetach ($\tau_a \ll \tau_d$) and the full line represents the model which takes into account the competition between dissociative attachment and autodetachment.

DISCUSSION

We have measured, as shown in Figures 3 and 4, the rate of production of SF_5^- ions in the reaction



as a function of the internal energy E_v (or temperature) of the parent molecule SF_6 above the threshold. Although it has been shown² that for certain values of their internal energy, SF_6^- ions can absorb CO_2 laser radiation, we rule out the possibility of the reaction $\text{SF}_6^- + h\nu \rightarrow \text{SF}_5^- + \text{F}$ because the interaction region between the excited neutral SF_6 beam and the argon Rydberg atoms are distinct. Moreover, the interaction time between the laser beam and the electrically accelerated SF_6^- ions would be too short.

We first used the spectroscopic values of Nowack and Lyman to fit our data with the only adjustable parameter E_d , ignoring the autodetachment level ($E_c \rightarrow \infty$). The dotted lines in Figure 4 correspond to the best fit with $E_d = .53$ eV. This value is in good agreement with other values determined by several authors^{8,18,19,23} if we assume a mean stabilization energy ΔE of .1 eV. The dip which appears is due to a lack of overlap between the *P*, *Q* and *R* branches, irrespectively of the value of E_d . When we introduce the modification of the effective rotational constant as a function of vibrational energy [Eq. (5)], the model correctly predicts the behaviour of the SF_5^- signal enhancement as a function of temperature for the CO_2 laser lines from *P*20 to *P*26. For the CO_2 laser lines, *P*28 and above, the model which ignores the autodetachment, predicts too large a signal at high temperatures. When we adjust the value of the energy E_c at which the autodetachment channel takes over the dissociative channel, we obtain a reasonably good agreement with the experimental values (Figure 7) with $E_c = 8500 \text{ cm}^{-1}$.

Using this model, and the spectroscopic values of Table I, we can estimate the relative absorption of the different CO_2 laser lines as a function of the excitation energy of the SF_6 molecule, for different temperatures. Since, under 1650 cm^{-1} , our model considers the vibrational states as discrete, the absorption spectrum is only represented above this value (this value of 1650 cm^{-1} is arbitrary and is chosen for computational purposes).

TABLE I
Numerical values used in the spectroscopic and collision models.

Frequency of the $\Delta\nu_3 = 1$ transition originating from the ground state	$\nu_0(0)$	=	947,988 cm ⁻¹
Ground state rotational constant	B_0	=	0.0906 cm ⁻¹
Anharmonic constant	X_{33}	=	- 1.74 cm ⁻¹
Coriolis constant	ζ	=	0.703
Dependence of the rotational constant upon vibrational energy E_v (in cm ⁻¹)	B'	=	$B'' - \alpha$
Threshold energy of the dissociative reaction SF ₆ ⁻ → SF ₅ ⁻ + F	E_d	=	$1.8 \cdot 10^{-4} + 3.5 \cdot 10^{-7} E_v$
Critical energy above which autodetachment dominates dissociative attachment	E_c	=	1.05 eV

We give only a single example of the discrete absorption spectrum (Figures 8 and 9).

CONCLUSION

We consider here a reaction between SF₆ molecules excited with 3 – 10 vibrational quanta, and very low energy electrons. This reaction can be thought of as a probe of the spectroscopic properties of this spectral region of SF₆, situated between the well-known fundamental transition of ν_3 and the very highly excited vibrational states. This region is, in fact, the one which was considered, in earlier works on isotope separation,¹ as connecting the resonant ν_3 ladder and the quasi-continuum leading to neutral dissociation.

We found that the Nowack and Lyman⁹ model correctly describes the absorption of the CO₂ laser in this excitation region if we take into account a modification of the anharmonicity constant, recently measured, and if we introduce the variation of the effective rotational constant as a function of the vibrational energy.

Our experimental measurements with a well-defined electron energy distribution together with a spectral analysis, confirm the accepted value of .43 eV. for the energy threshold of the dissociative reaction SF₆⁻ → SF₅⁻ + F, as opposed to the value of 0.2 eV determined by Chen and

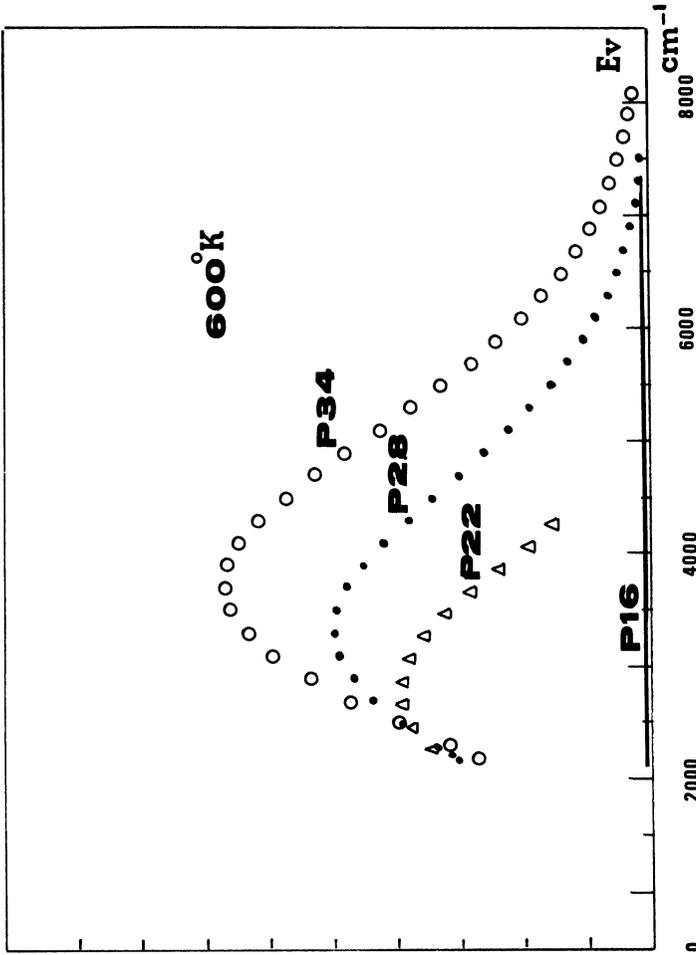


FIGURE 8 Absorption spectrum of the quasi-continuum of SF₆ as predicted from the spectroscopic model for a SF₆ temperature of 600°K and for different CO₂ laser lines. The important contribution of the discrete levels (below 2000 cm⁻¹) is not represented.

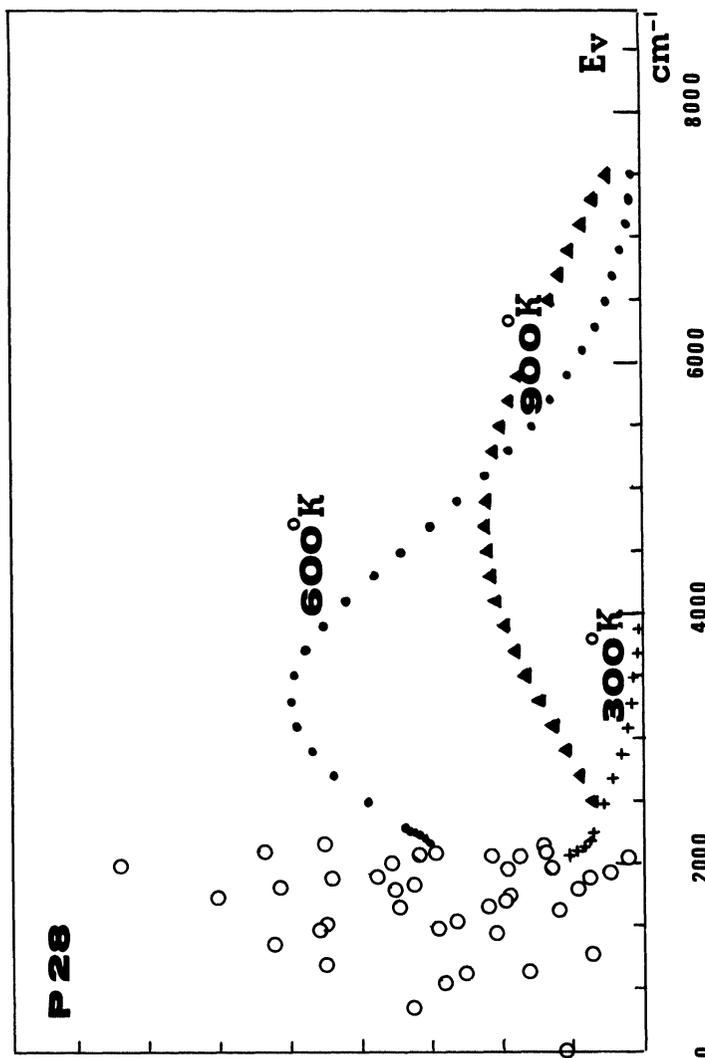


FIGURE 9 The discrete absorption and quasi-continuous spectrum of SF₆ for the P28 CO₂ laser line is given at 600°K as predicted from the spectroscopic model. Only the quasi-continuous part of the spectrum is represented for 300°K and 900°K for the P28 CO₂ laser line.

Chantry. This discrepancy is most probably due to the high energy tail of the electron energy distribution used in their experiment. We conclude, from our spectral analysis that the absorption process responsible for the laser enhancement of the dissociative channel is a single photon absorption. We also show that this dissociative process is dominated by an autodeachment channel above a given internal energy of the negative ion that we estimate.

This study of the reaction process which occurs in a collision between an atom in a Rydberg state and a molecule is an example of more general kind of reactions between excited atoms and molecules which can be described as three step processes, the first involving the formation of negative ion by means of a shape or Feshbach resonance,²⁴ the second, a stabilization process and the third, competition between several dissociating processes of the negative ion.

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