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ANALYSIS OF DISSOCIATION PROCESES THROUGH INTERFEROMETRIC STUDIES OF VT RELAXATION TIMES

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Analysis of Dissociation Processes through Interferometric Studies of VT Relaxation Times

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5. Atomic and Molecular Physics

Abstract

In this communication we describe a simple method for obtaining useful information on laser-induced dissociation processes of polyatomic molecules by studying VT relaxation in a regime of strong laser excitation. Our studies were carried out by using an interferometric technique. We also briefly outline a theoretical analysis of VT relaxation times in the presence of dissociation.

1. Introduction.

In a number of experimental papers [1,2,3] it was established that multiphoton dissociation processes (MPD) of a variety of molecules can be induced by a high-power, pulsed CO_2 laser. In particular, in SF_6 a laser fluence of $\sim 1\ J/cm^2$ is sufficient for MPD to occur [4]. Experimentally, the usual approach has been to irradiate a low-pressure gas medium in a sample cell with CO_2 laser pulses, and analyze the gas, before and after the irradiation, by infrared absorption and mass spectroscopy. More recently, a crossed laser and molecular beam method has been developped, with a direct identification of the dissociation products through a mass-spectrometer [5].

In this paper we describe a simple method of detecting and obtaining useful information on dissociation processes of polyatomic molecules by studying VT relaxation processes. In case of strong laser excitation, one observs non-linear vibrational relaxation effects, i.e., the nature of relaxation processes depends on the rate of excitation [6]. In particular, our results indicate that the VT relaxation time shows a dramatic decrease in correspondence of the occurrence of dissociation of highly excited molecules. Thus, an accurate analysis of the dependence of the VT relaxation time on laser fluence can signal the onset of dissociation of the molecules under investigation.

We apply the above method to SF_6 molecules, and briefly outline a theoretical analysis providing an expression of the VT relaxation time in the presence of dissociation.

2. Experimental Apparatus and Technique.

In our experiments we used the phase-fluctuation optical heterodyne (PFLOH) technique [7], which consists of coherently detecting the small phase change of a single-frequency laser beam, which results when it passes through a transparent medium whose density and, consequently, refractive index have been changed by energy absorption.

A full description of our experimental setup is given in ref. [8]. Here, we shall limit ourselves to say that we used a Mach-Zender interferometer. A cell containing the gas sample under investigation was placed in one arm of the interferometer, which was illuminated with a single-frequency He-Ne laser (Coherent, mod. 2000). The excitation laser was either a CW CO_2 laser (Apollo Inc., mod. 560), used in Q-switch mode, or a TEA CO_2 laser (Lumonics, mod. K-203), so as to have a broad range of input energies (0.001 - 2.6 J/cm^2). The gas cell was enclosed by two Brewster Zn-Se windows, transparent to both visible and 10.6 μm radiation. Both CO_2 and He-Ne laser beams overlapped in the sample zone: the CO_2 beam inducing the refractive index change, and the He-Ne laser beam probing it. A photodiode detected the heterodyned beams.

A more thourough discussion of the PFLOH technique and of a number of conditions which have to be satisfied in order to apply it, is also given in ref. [8]. We limit ourselves to note that in the interferometric method, which shows a very high sensitivity and allows one to carry out measurements on a large range of experimental parameters (gas pressure and temperature, exciting laser energy, etc.), the measured quantity is the phase change difference $\Delta\phi(t)$ between the laser beams in the two arms of the interferometer:

$$\Delta\phi(t) = (2\pi\ell/\lambda)(n_o - 1)(\Delta T/T_o) \quad , \qquad (1)$$

where ℓ is the cell length, λ the He-Ne wavelength, ΔT the temperature variation, T_o and n_o the initial gas temperature and refractive index at $T = T_o$, respectively.

3. Experimental Results.

By using the apparatus described above, we carried out a set of experiments on VT relaxation times in pure SF_6 and SF_6-Ar mixtures.

In the SF_6 molecule the absorption of IR laser photons takes place through the triply degenerate ν_3=965 cm^{-1} vibrational mode, while the VT relaxation process is characterized by a single relaxation time of the ν_6 mode, which has the lowest quantum energy (363 cm^{-1}). This is true at very low excitation energy, and, in this case, for the relaxation time one has, approximately, τ_{VT}= 110/p (μs/torr), where p is the gas pressure.

Figure 1(a) shows an oscillogram of $\Delta\phi(t)$ for 0.5 torr of pure SF_6 in the case of low excitation energy (∼60 mJ/cm^2). The relative relaxation time (120 μs ± 20 μs) is fairly constant, thus confirming a single-mode (ν_6) relaxation model for SF_6.

On the contrary, at higher excitation energies the relaxation time begins to exhibit a nonlinear behaviuor: it shows a strong time dependence and , moreover, it is a function of the optical excitation energy or of the corresponding initial (just after laser irradiation) vibrational temperature of the molecules (T_v). A typical example is given in fig.1(b), where the oscillogram of $\Delta\phi(t)$ is reported for the same conditions of case (a), but for an energy fluence of 2J/cm^2. In this case the relaxation process is not characterized by a single relaxation time, and one can define an effective relaxation time τ_{eff}, i.e., the time in which the initial deviation of the gas temperature from the equilibrium value changes by a factor 1/e. In fig. 1(b) $\tau_{eff} \simeq$ 40 μs ± 5 μs.

Finally, in fig.2 the effective value τ_{eff} of the VT relaxation time is reported as a function of the initial vibrational temperature of the SF_6 molecules (p=0.5 torr). The corresponding laser fluence values (F), relative to actual measurements, are also reported. The points of fig.2 are only a fraction of a large number of measurements, carried out at different pressures and laser fluences, but all showing the same trend: the relaxation time is a strongly decreasing function of the excitation energy.

The anharmonicity of individual modes, and gas heating (Landau-Teller effect) can cause non-linearities in the thermalization of excited molecular gases, as already known [6] . Our experimental results confirm the above theoretical findings, and, moreover, show a new, very interesting feature, never seen before: a further dramatic decrease in the relaxation time at very high excitation energies (0.5 J/cm^2), as seen from the curve of fig.2. We relate this behaviour to the onset of an efficient dissociation process of the highly vibrationally excited SF_6 molecules.

Our experimental results are in good agreement with the results obtained in the following section, where a theoretical analysis of the dependence of the VT relaxation time on dissociation processes is briefly discussed. Moreover, they are also in good agreement with the calculations reported by Panchenko in a recent theoretical work [9], where he showed that also a partial dissociation of the vibrationally excited molecules causes a non-linear behaviour of VT energy exchange, with a consequent decrease of the relaxation time as a function of the initial vibrational temperature.

4. Theoretical analysis and conclusions.

In this section we give a brief outline of our analysis of VT relaxation times in the presence of dissociation processes induced by VV exchange between highly vibrationally excited molecules, postponing a more detailed discussion to a forthcoming paper [10] .

We analyze a system of anharmonic oscillators vibrationally excited by intense laser radiation (10.6 μm) almost resonant with the first vibrational level of the IR active mode of the molecules (ν_3 for SF_6). In order to take into account dissociation processes, the oscillator energy is truncated to the mth level, i.e., we assume x_{m+1}= 0, where x_n is the vibrational distribution function of the nth level; m=35 for SF_6 [11]. Thus, a fraction of the molecules will spend its energy for dissociating.

Since the VV and VT relaxation processes are temporally well separated ($\tau_{VT} \gg \tau_{VV}$), for the average number α of vibrational quanta per molecule we can write:

$$\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_{VV} + \left(\frac{d\alpha}{dt}\right)_{VT} , \qquad (2)$$

where $\alpha = (\sum_{n=o}^{m} nx_n)/(\sum_{n=o}^{m} x_n)$. One can show that [10] :

$$\left(\frac{d\alpha}{dt}\right)_{VV} = -K_d(m - \alpha) , \qquad (3)$$

where the dissociation constant K_d is given by

$$K_d = Q_{01}^{10} \frac{(m + 1)\, e^{mw}}{(\sum_{n=o}^{m} e^{nw})(\sum_{n=o}^{m} e^{nz})} f(m) , \quad f(m) = \sum_{i=o}^{m} \left\{ i \exp\left[\frac{iE_1}{kT_v} + (i - 1)\delta - (i - 1)\frac{2\Delta E}{kT} \right] \right\} . \qquad (4)$$

In eq.(4) $Q_{n+1,n}^{m-1,m} = (n+1)\, mQ_{10}^{01} \exp -(2\Delta E/kT)(m-n-1)$ is the probability of one quantum vibrational exchange [12], $E_1 = h\nu_3$ (in SF_6), k the Boltzmann constant, δ the parameter of molecular anharmonicity [10,12], ΔE the anharmonic defect, and T the gas translational temperature. Finally, $z = (-\delta + (2\Delta E/kT) + E_1/kT_v)$, and $w = (\delta - (2\Delta E/kT) + E_1/kT_v)$.

Moreover, one has [10] :

$$\left(\frac{d\alpha}{dt}\right)_{VT} = -\frac{\alpha - \alpha_{eq}}{\tau_{VT}^{A}} , \quad \tau_{VT}^{A} = \tau_{VT}\left[\frac{1 - \exp(\delta - E_1/kT_v)}{1 - \exp(- E_1/kT_v)}\right]^2 , \qquad (5)$$

where α_{eq} is the value of α for $T=T_v$, τ_{VT} is the VT relaxation time at very low excitation defined in section 3 (τ_{VT}=110/p), and τ_{VT}^{A} the value obtained taking into account the Landau-Teller effect and the anharmonicity of the individual modes [12]. Thus, defining an effective relaxation time as $\tau_{eff} = |(\alpha - \alpha_{eq})/(d\alpha/dt)|$, we can write:

$$\tau_{eff} = \frac{\tau_{VT}^{A}}{(1+\chi)} , \qquad \chi = K_d \frac{(m-\alpha)}{\alpha - \alpha_{eq}} . \qquad (6)$$

In absence of dissociation processes, χ =0 and τ_{eff} reduces to the value τ_{VT}^{A} of eq.5.

Figure 3 shows the theoretical calculation of τ_{eff}, through eq.6, as a function of the initial vibrational temperature for 0.5 torr of SF_6, with (curve a) and without (curve b) dissociation processes taken into account. The values of τ_{eff} are normalized to τ_{VT} ($\simeq$220 μs for 0.5 torr of SF_6). m=35, δ = 0.15, and ΔE=2°k are the best-fit values used in the theoretical calculation of fig.3. We have checked the curves of τ_{eff} against different sets of the above molecular parameters, always obtaining the same qualitative behaviour. For sake of comparison, we have also reported the measured values of τ_{eff} for 0.5 torr of SF_6 (see fig.2).

As easily seen, when dissociation processes are taken into account (curve a), the calculated value of τ_{eff} shows a strong decrease at high vibrational temperatures (corresponding to strong laser excitation). No similar effect is shown in case b (no dissociation). Thus, the results of our theoretical model fully confirm the effect of dissociation processes on VT relaxation times, as observed experimentally.

In conclusion, in this paper we have analysed, both experimentally and theoretically, the influence of dissociation processes on VT relaxation times in polyatomic molecules. In particular, we have shown that the beginning of dissociation processes of the highly vibrationally excited molecules causes a strong decrease of the VT relaxation time, well beyond the decrease brought about by the Landau-Teller mechanism and the effect of the anharmonicity of individual vibrational modes. A full description of our theoretical model is the subject of a forthcoming paper [10].

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FIGURE CAPTIONS.

Fig.1 : Oscillogram of $\Delta\phi(t)$ for 0.5 torr of SF_6 with a laser fluence of (A) 60 mJ/cm^2, and (B) 2 J/cm^2. The baseline passes through the peak on the left.

Fig.2 : The effective relaxation time τ_{eff} as a function of the initial molecular vibrational temperature T_v (0.5 torr of SF_6). Laser fluence values (F), corresponding to actual measurements, are also reported.

Fig. 3 : Theoretical calculation of τ_{eff}, normalized to τ_{VT}= 220 μs, as a function of T_v for 0.5 torr of SF_6 with (curve a), and without (curve b) dissociation (m=35, δ=0.16, ΔE=2°K). Full dots represent experimental values of τ_{eff}.

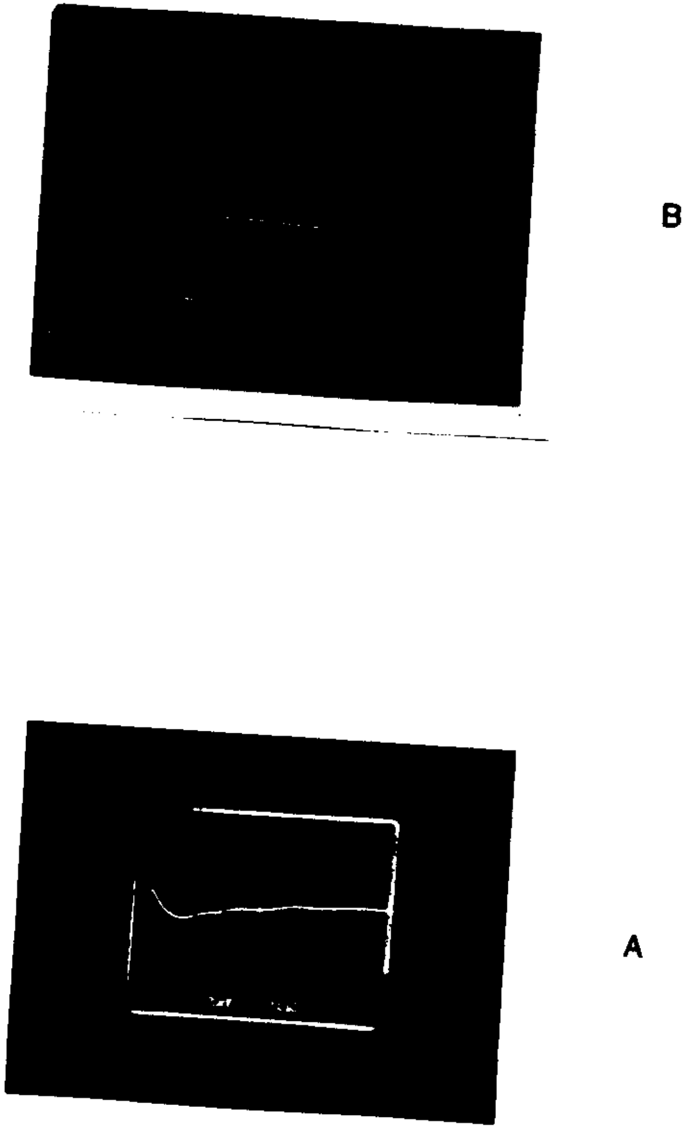
B
A

Fig.1

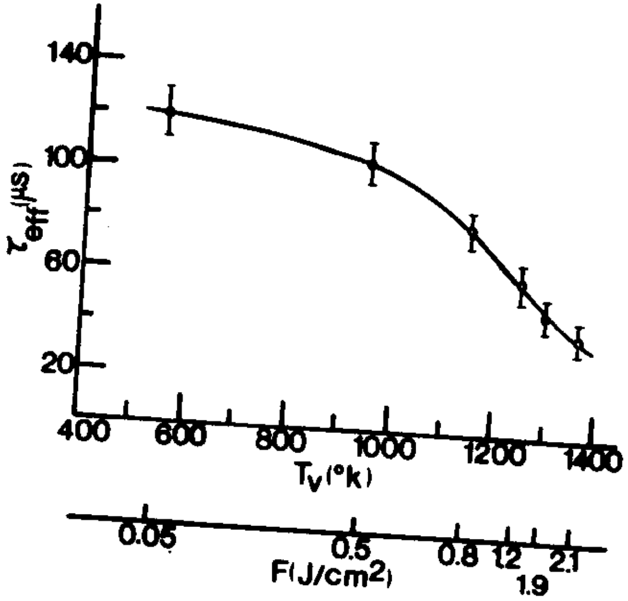
τ_{eff} (μS)
140
100
60
20
400
600
800
1000
1200
1400
T_V (°k)
0.05
0.5
0.8
1.2
1.9
2.1
F (J/cm^2)

Fig. 2

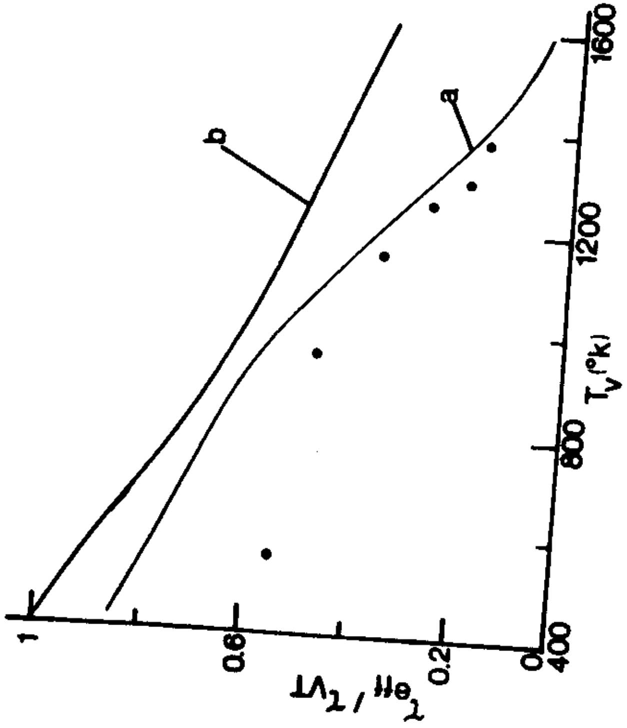

Fig.3

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INTERFEROMETRIC STUDIES OF VT RELAXATION TIMES IN A REGIME OF STRONG LASER EXCITATION

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Abstract—In this paper we describe the analysis of non-linearities in the vibrational relaxation rates of SF_6 molecules in a regime of strong laser excitation. Our studies were carried out using an interferometric technique which is particularly suitable to the investigation of the time dependence of VT relaxation times in molecular systems. At very high excitation energies a dramatic decrease in the VT relaxation time was found. This behaviour is related to the beginning of multiphoton dissociation processes of SF_6 molecules.

1. INTRODUCTION

Investigation of the mechanisms of transformation of the optical excitation energy by molecules and molecular complexes is undoubtedly one of the central problems in the physics of resonant interaction of laser radiation with matter. In particular, both studying vibrational relaxation processes and a precise knowledge of relaxation times for molecular systems are of great interest in laser photophysics and photochemistry.

A very interesting aspect of the research on vibrational relaxation is the investigation of the decay of strongly excited states. Many-photon dissociation of polyatomic molecules was achieved by using IR and NIR lasers.(1, 2) In cases of such strong excitation there are non-linear vibrational relaxation effects,(3) i.e. the nature of relaxation processes may depend on the rate of excitation. Furthermore, highly excited systems can have new relaxation processes, and this is true of intermolecular as well as intramolecular relaxations.

The dependence of the rate of vibrational relaxation on the excitation intensity may have a considerable influence on many photophysical and photochemical processes. For example, such effects are particularly important in many-photon dissociation of molecules in the presence of collisions.(4)

In this paper we describe the analysis of non-linearities in the vibrational relaxation rates of SF_6 molecules in a regime of strong laser excitation. To carry out these studies we used the phase-fluctuation optical heterodyne (PFLOH)(5) technique, which is particularly suitable to the investigation of the time dependence of VT relaxation times in molecular systems. The PFLOH technique consists of coherently detecting the small phase change of a single-frequency laser beam which results when it passes through a transparent medium whose density and, consequently, refractive index have been changed by energy absorption. This technique has been used successfully for studying microwave absorption characteristics of liquids,(6) for trace detection in the gas phase(7) and for selective, non-destructive gas chromatography.(8)

In section 2 we describe our experimental apparatus and technique. The experimental results are shown in Section 3. Finally, in Section 4, we discuss our findings.

2. EXPERIMENTAL SETUP AND TECHNIQUE

A schematic view of our experimental apparatus is shown in Fig. 1. The Mach–Zehnder interferometer consists of two cubic beam-splitters (BS), which are less sensitive to acoustic noise, two Ge windows (W), with 10.6 μm anti-reflection coating, and a Babinet–Soleil phase compensator (B-SC). The excitation laser was either a CW CO_2 laser (Apollo Inc., model 560) used in Q-switch mode or a TEA CO_2 laser (Lumonics, model k-203), so as to have a broad range of input energies (0.01–1.6 J/cm²). The laser beam, directed and gently focused by a system of Au mirrors (M), entered and left the interferometer via the two Ge windows which, although transparent at 10.6 μm, formed two of the high-reflective visible mirrors of the interferometer. The Mach–Zehnder interferometer was

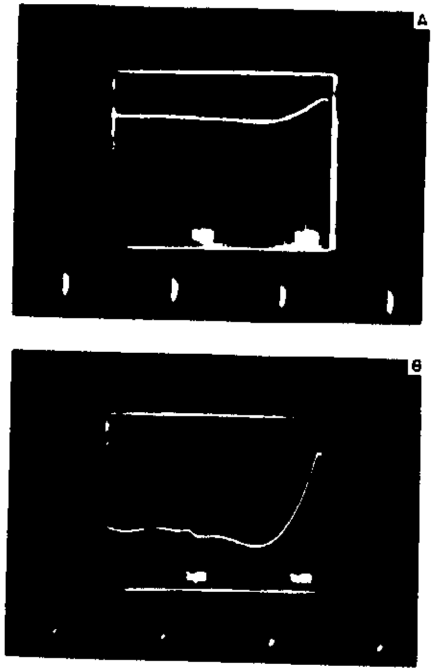

Fig. 2. Oscillogram of $\Delta\phi(t)$ for an SF_6–Ar mixture (0.1 : 4 torr) with a laser energy fluence of (a) 50 mJ/cm² and (b) 1 J/cm².

4. DISCUSSION AND CONCLUSIONS

The anharmonicity of individual modes and gas heating can cause non-linearities in the thermalization of excited molecular gases, as already known.(3) The anharmonicity of molecular vibrations has the effect that even in the case of diatomic molecules the thermalization of a gas as a result of the VT relaxation is non-exponential: the characteristic thermalization time depends strongly on the energy absorbed by the gas.(11) The resulting heating of the gas accelerates the VT relaxation process in accordance with the Landau–Teller mechanism.

Our experimental results confirmed the above theoretical findings, but showed a new, very interesting feature never seen before: a further dramatic decrease in the relaxation time at very high excitation energies ($\simeq 16$ mJ/cm³), as can be seen from the curve of Fig. 5. This behaviour can be related to the beginning of an efficient multiphoton dissociation process of SF_6 molecules.

Fig. 3. Correlation between the laser energy fluence (J/cm²), the energy absorbed by the gas (mJ/cm³) and the corresponding average number of photons (⟨n⟩) absorbed per SF_6 molecule (for 2 torr of pure SF_6).

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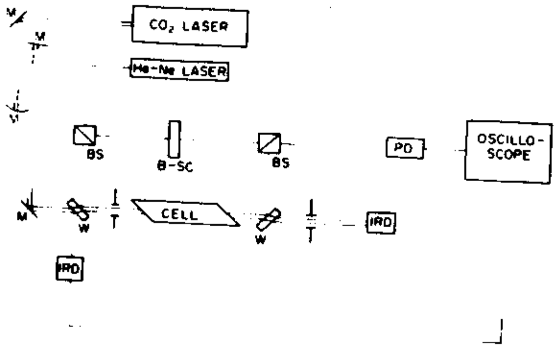

Fig. 1. The experimental setup

illuminated with a single-frequency He–Ne laser (Coherent, model 200). A cell containing the gas sample under investigation was placed in one arm of the interferometer. The cell was enclosed by two Brewster ZnSe windows, transparent to both visible and 10.6 μm radiation. Both CO_2 and He–Ne laser beams overlapped in the sample zone: the CO_2 beam inducing the refractive index change, and the He–Ne laser beam probing it. IR detectors (IRD) were used to monitor the CO_2 laser intensity, while a photodiode (PD) detected the heterodyned beams.

In the interferometric method, which shows a very high sensitivity and allows one to carry out measurements on a large range of experimental parameters (gas pressure and temperature, exciting laser energy, etc.), the measured quantity is the phase change difference $\Delta\phi$ between the laser beams in the two arms of the interferometer [see Ref. (3) for a full description]:

$$\Delta\phi(t) = (2\pi l/\lambda)(n_0 - 1)(\Delta T/T_0), \tag{1}$$

where l is the cell length, λ the He–Ne wavelength, ΔT the temperature variation, T_0 the initial gas temperature and n_0 the refractive index at $T = T_0$.

By using this method for studying the temporal evolution of VT relaxation rates, there are a number of conditions to be satisfied which restrict the values of l and p (the gas pressure in the cell) to be used. Firstly, the cell length and pressure have to be selected so that measurements of the phase difference $\Delta\phi$ due to the heating of the gas during the relaxation time satisfy the condition $\Delta\phi \ll \pi$. In this case the working point is located on the linear part of the interferometer characteristic and the determination of the intensity in the field of the interference pattern is proportional to the change in the phase difference.

Secondly, the experimental conditions have to be selected so that the diffusion of heat can be ignored in the analysis of the experimental data:

$$\tau_c \simeq w^2/(4k_d) \gg \tau, \tag{2}$$

where $w/2$ is the beam radius in the cell, k_d the thermal diffusion coefficient, τ_c the thermal diffusion time and τ the characteristic VT relaxation time. Equation (2) ensures that gas cooling takes place on a time scale which is much slower than that relating to the relaxation process. Since τ is inversely proportional to p, this condition limits the minimum value of the sample pressure to be used.

Finally, a possible source of error in the interferometric method for the determination of the relaxation time τ is the delay between the establishment of the density (pressure) in a gas and the establishment of its temperature. This acoustic delay is governed by a characteristic time given by

$$\tau_{ac} \simeq w/v_{ac}, \quad v_{ac} = \gamma(R/m)(T)^{1/2}, \tag{3}$$

where c is the sound velocity in the gas, $\gamma = c_p/c_v$, R is the gas constant and m the molecular mass. Obviously, in order to have correct experimental results, the condition $\tau_{ac} \ll \tau$ has to be satisfied.

If the above conditions are satisfied it can be shown[3,9] that the relaxation time can be obtained from the following equation

$$1/\tau = \{\ln[\psi(t + \Delta t)] - \ln[\psi(t)]\}/\Delta t, \tag{4}$$

where

$$\psi(t) = \frac{\left|\frac{v_t - v_{t0}}{v_{t0}}\right| \left(\frac{1}{1 - Bv_{t0}}\right)}{1 + \left|\frac{v_t - v_{t0}}{v_{t0}}\right| \left(1 - \frac{1}{1 - Bv_{t0}}\right)}. \tag{5}$$

In equation (5), $v_t(t)$ and v_{t0} are the instantaneous value and the total variation of the heterodyned signal from the photodiode (read on the oscilloscope), respectively. The quantity B is a constant which depends on experimental conditions and interferometer characteristics.

Finally, in order to avoid gas contaminations in the cell, vacuum levels of the order of 10^{-6} mb were obtained before carrying out the experiments, by using a diffusion pump (Edwards, model diffstak 100-300).

3. EXPERIMENTAL RESULTS

By using the apparatus described above we carried out a set of experiments on VT relaxation times in pure SF_6 and SF_6–Ar mixtures. Our results confirmed the results of Ref. (3), and extended them to the high excitation energy regime.

In the SF_6 molecule (a spherical top) the absorption of IR laser photons takes place through the triply degenerate $v_3 = 965\,cm^{-1}$ (F_{1u}) vibrational mode. Moreover, experimental results suggest that the energy of laser radiation absorbed in SF_6 is distributed between all the modes in a time $\simeq 1\,\mu s \cdot torr$[10] and, subsequently, the VT relaxation process is characterized by a single instant of the mode v_6 (F_{2u}), which has the lowest quantum energy ($363\,cm^{-1}$). This is true at low excitation energies and, in this case, for the relaxation time one has $\langle\tau\rangle = 100\,p$ (μs torr), where p is the SF_6 pressure and $\langle\ \rangle$ means "at low excitation energy".

Figure 2(a) shows an oscillogram of $\Delta\phi(t)$ for 0.1 torr of SF_6 in a rare gas (Ar) thermostat (4 torr), in the case of a very low excitation energy ($50\,mJ\,cm^{-3}$). The relative relaxation rate $\langle\tau\rangle$ ($90 \pm 10\,\mu s$) is fairly constant, thus confirming a single-mode (v_6) relaxation model for SF_6.

On the contrary, at higher excitation energies τ begins to show a non-linear behaviour: it shows a strong time dependence. This can be seen in Fig. 2(b), where the oscillogram of $\Delta\phi(t)$ is reported for the same SF_6–Ar mixture of Fig. 2(a), but for an energy fluence of $1\,J\,cm^{-2}$. In this case the relaxation process is not characterized by a single relaxation time, and one can define an effective relaxation time $\bar{\tau}$, i.e. the time in which the initial deviation of the gas temperature from the equilibrium value changes by a factor of 1/e. In Fig. 2(b) $\bar{\tau} \simeq 60\,\mu s$.

To aid comprehension of the following results, in Fig. 3 we correlate the laser energy fluence ($J\,cm^{-2}$) to the energy absorbed by the gas ($mJ\,cm^{-3}$), and to the corresponding average number of $10.6\,\mu m$ photons ($\langle n\rangle$) absorbed per SF_6 molecule.

Figure 4 reports the time dependence of the normalized vibrational relaxation time $\tau/\langle\tau\rangle$ for 2 torr of pure SF_6 (in this case $\langle\tau\rangle = 50\,\mu s$), with the energy absorbed per cm^3 as a parameter. As is easily seen, the relaxation time at higher excitation energies is much shorter than the corresponding $\langle\tau\rangle$, and shows a strong time dependence. Moreover, it is a function of the optical excitation intensity or of the corresponding initial vibrational temperature of the molecules.

Finally, in Fig. 5, which is a summary of our results, the effective value ($\bar{\tau}$) of the VT relaxation time is reported as a function of the laser excitation energy, $E_v(0)$, absorbed per cm^3: $\bar{\tau}$ is a decreasing function of the excitation energy. A very interesting feature of our results, never seen before, is the dramatic decrease of the relaxation time at very high excitation energy ($16\,mJ\,cm^{-3}$, corresponding to a laser fluence of $1.6\,J/cm^2$). This feature will be discussed in the next section.

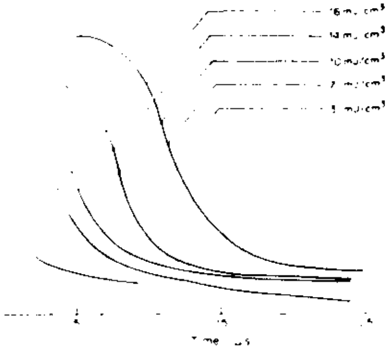

Fig. 4. Time dependence of the normalized vibrational relaxation time ($\tau/\langle\tau\rangle$) for 2 torr of pure SF_6, with the energy absorbed per cm^3 as a parameter.

Multiphoton dissociation of SF_6 molecules was observed[12] by using CO_2 laser radiation pulses with energy fluence values ($\simeq 1\,J\,cm^{-2}$) very close to the ones used in our experiments. Moreover, in a recent theoretical analysis[13] Panchenko obtained an expression for the effective relaxation time of VT energy exchange in the presence of dissociation processes. He showed also that a partial dissociation of the vibrationally excited molecules causes the non-linear behaviour of VT relaxation times. Numerical computations of his equation for the effective relaxation time proved to be in very good agreement with our experimental curve (see Fig. 5). Thus, our results represent the first experimental confirmation of the supposed influence of dissociation processes on VT relaxation times. Further work on this point is in progress.

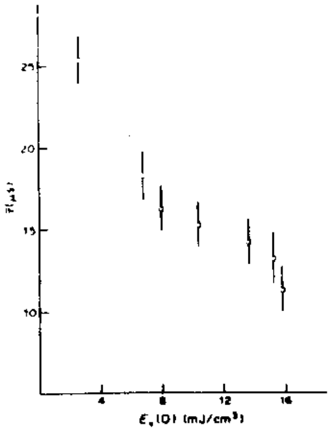

Fig. 5. The effective relaxation time $\bar{\tau}$ as a function of the laser excitation energy, $E_v(0)$, absorbed per cm^3 (2 torr of pure SF_6).

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EXPERIMENTAL AND THEORETICAL ANALYSIS OF RESONANT MULTIPHOTON IONIZATION OF BENZENE

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ABSTRACT

A multi-photon ionization (MPI) apparatus utilizing a time of flight mass spectrometer as parent and fragment ions detector is described. Results regarding the multiphoton resonant ionization and fragmentation of benzene are presented together with an accurate numerical evaluation of the photoionization probability. The comparison between our experimental and numerical results offers the possibility of estimating the value of the two-photon ionization cross section from the $^1B_{2u}$ excited state of benzene, not yet established.

PACS Numbers: 3380 E (Photoionization),
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I. INTRODUCTION

The multiphoton ionization (MPI) technique[1,2] makes use of a strongly focused (up to the diffraction limit) light beam for reaching power densities so high to enhance the process of multiphoton absorption by molecules and consequent ionization, which takes place with considerable rate.

When the laser wavelength is tuned, a number of resonance enhanced ion yields, corresponding to resonant absorption of two or more photons, can be observed, so that a real multiphoton ionization spectrum can be obtained. This technique has proved very efficient in molecular spectroscopy of electronic states, particularly those forbidden to single photon transitions[3,4].

Due to the known properties of resonant phenomena, this ionization technique can provide ions of any chemical species only at very well defined energy values ($\Delta E/E \simeq 10^{-3}$) and, therefore, can prove very useful where highly selective ionization is required.

If molecular photoions are thus produced inside the ion source of a mass spectrometer[5-10], a mass spectrum of the photoproducts (parent and/or fragment ions) and an optical absorption spectrum are simultaneously obtained. In such MPI mass spectrometers the mass spectrum of a molecular mixture is strongly dependent on the wavelength of the ionization radiation thus allowing evidence of the different chemical substances even if present in trace concentrations.

The analysis of the ionization yield dependence on laser beam fluence can provide a host of information on the kinetics of formation of photoions. In particular, while in ordinary multiphoton laser isotope separation processes the fotoionization yield is proportional to $I^{1.5}$, where I is the laser intensity[11], in the case of benzene one observes a more complicate dependence on I, which can be approximated with a power law of the form I^2 (ref.12) or I^3 (present work), according to the intermediate level used for ionizing the molecules. The different behavior of benzene can be easily explained with a simple kinetic scheme, illustrated in the following of this paper, in which the Gaussian spatial distribution of the focused beam is taken into account. By using this model, all the experimental data relative to two different vibronic resonance lines (4716 Å and 4819 Å) of benzene are shown to fit nicely with the theoretical curve.

The above result can be instrumental for assessing the order of magnitude of the two-photon ionization cross-section σ_2 of the benzene from the $^1B_{2u}$ excited level, not yet well known in literature. The value so obtained ($\simeq 4\times10^{-47}$ cm^4. sec) is quite distant from the value $\simeq 10^{-41}$ cm^{4}sec obtained in ref. 12 with an approximate order of magnitude analysis. It is noteworthy that our value is much closer to typical two-photon absorption cross-sections (10^{-50} cm^{4}sec) reported by several other authors[13].

The peculiarity of the benzene photoionization stems from the very high value of the relaxation rate γ of the intermediate level $^1B_{2u}$, which inhibits the achievement of complete

saturation of the photoionization process. By contrast, the photofragmentation observed in laser isotope separation schemes exhibits, approximately, a stepwise dependence on power density, thus originating the commonly observed 1.5–power law. In particular, the γ value for the $^1B_{2u}$ level becomes quite large for vibronic lines lying more than 3000 cm^{-1} from the 0–0 band. This circumstance has been exploited in the present experiment by choosing the 4716 Å and 4819 Å lines for carrying out the theoretical analysis.

The organization of this paper is as follows. A detailed description of the time of flight (TOF) mass spectrometer with a MPI ion source is given in the next section (II). The experimental results obtained in the study of benzene molecule are given in section III. Finally, in section IV an accurate numerical evaluation of the photoionization yield is carried out, by using a rate equation approximation for the benzene level populations and a Gaussian pattern for the focused laser beam.

II. EXPERIMENTAL SET-UP

The apparatus is schematically represented in Fig. 1(a). A grating tuned oscillator-amplifier dye laser (Lambda Physik FL 2000) pumped by a nitrogen laser (EMG 101, 700 KW peak power, 20 pps repetition rate) generates tunable radiation having a linewidth of 1 cm^{-1}; the output peak power is about 60 KW, constant over the wavelength range used in our experiment (460 ÷ 495 nm). The wavelength resolution is 0.01 nm; the beam is

focussed to a waist size of about 15 μm with a power density $I_{max} \simeq 10^{10}$ W/cm^2. The laser pulse duration is 12 ns FWHM. The temporal evolution of the laser pulse was monitored during the experiments by using a fast photodiode collecting a small fraction of light scattered from the dye laser: the pulse shows a very fast rise time (1 ns), followed by a constant output power, and a slower (~ 1.5 ns) tail. This justifies the assumption of section IV where the laser pulse is approximated by a step function of constant height for 10 ns.

A stainless steel vacuum chamber, kept at a working pressure of $10^{-6} \div 10^{-4}$ Torr (after baking at 200 ÷ 300 °C to the residual pressure of 10^{-8} Torr),contains the gas inlet G, the ion source I, the drift tube T and the ion detector D. The gas inlet G is made of a 20 μm glass needle injector fed by a variable, programmable self controlling leak. The light beam enters the vacuum chamber through the window W and is strongly focussed by the two lens system L into the ion source I of the mass spectrometer.

The TOF spectrometer is similar to that previously used by some of us in experiments of dissociative ionization induced by electron impact[14,15]. The ion source is a three gap model (see Fig. 1(b)). In the region s (6 mm thick) ions are formed and pushed off by a static (450 V/cm) field through a narrow (2 mm diameter) hole, into the field-free region ℓ (0.8 mm thick, delimited by two tight grids). In region d (1 cm thick) ions are accelerated by a static voltage (1000 V) into the field-free drift tube T (40 cm long).

The ion detector D was built by assembling a focused dynode

EMI D233 detector and a venetian blind first dynode, in order to obtain both the high quality signal (risetime, pulse amplitude, pulse width, etc.) of a focused multiplier and the narrow spread of ions trajectories (≲ 2 mm) assured by the venetian blind shape dynode. A voltage of 2.5 KV is applied between the drift tube, delimited by grid A, and grid B in order to drastically accelerate ions and hence reduce the spread of times of flight; a small (50 V) positive voltage is applied between grid B and the first dynode, in order to push the just extracted electrons towards the multiplier dynodes.

In comparison to any commercial multiplier directly applied at the end of the drift tube, this assemblage allows a reduction of the peak widths of about a factor of two. For example, the experimental full width at half maximum of the CO_2^+ peak is 24 nsec, to be compared to the time (18 nsec) taken by ions of such mass and energy to travel the 2 mm path of the venetian-blind thickness, and to the laser pulse width (~ 12 ns).

Ions are detected and their time measured at the rate of one single ion per laser pulse; all the events in which more than one ion reach the detector within the chosen time window are rejected in order to prevent any discrimination against heavy masses. Moreover, the detector response throughout all the parent and fragment ions spectrum is mass independent and proportional to the relative abundances. All the difficulties connected with non-linear detector response and/or deconvolution of the output signal current are avoided.

The collection efficiency of the apparatus was evaluated by a Montecarlo program. Position, velocity components and instant of formation of the ions were randomly extracted; optimized values of the characteristic parameters (geometrical, electrical, etc.) of the apparatus to be introduced into the program were obtained through a number of best fits between experimental and calculated peaks of known masses. In this way collection efficiences ranging from 75% to 15% were found for ion kinetic energies ranging from 0.1 to 1.0 eV.

III. EXPERIMENTAL RESULTS

By using the above described apparatus we carried out a number of experiments on the benzene molecule (C_6H_6), because of its great physical and chemical interest.

A MPI scheme similar to that of Ref. 12 was used to ionize benzene molecules with visible photons: a two-photon resonant, 4 photon ionization process. Benzene ionization potential is 9.34 eV. Therefore, using a dye laser in the visible region (450 ÷ 500 nm), four photons are needed to excite a molecule into the ionization cotinuum. The overall process is characterized as a coherent two-photon excitation to the intermediate $^1B_{2u}$ state of benzene from the $^1A_{1g}$ ground state, followed by an incoherent two-photon excitation to the continuum (ionization).

A spectrum of the total ion yield as a function of laser wavelength is shown in Fig. 2. The spectrum has well defined structure. As is well known, the lowest excited state shows well resolved ro-vibronic structure. Thus, the wavelength spectrum of the total yield exhibits the "fingerprint" of the intermediate state. The two-photon absorption (TPA) bands of the S_0 (ground

state) $\longrightarrow S_1(^1B_{2u})$ transition are similar to the one-photon absorption (OPA) ones. The most intense peaks are members of a 925 cm^{-1} (totally symmetric breathing vibration mode, ν_1, of the benzene molecule) progression ($14^1_0 1^n_0$). Other well defined peaks belong to the $14^1 1^n_0 16^1_1$ progression. More generally, all the resonant peaks observed in our spectrum coincide with the ones observed in Ref. 16 by detecting the fluorescence from the two-photon excited $^1B_{2u}$ state. Other vibronic transitions (S_0-S_1) of lowest intensity are embedded in the background signal, which is due to non resonant four-photon ionization of C_6H_6 molecules. Finally, we note that the above spectrum was obtained with a gas pressure in the spectrometer of 1×10^{-5} torr.

A common feature of all the recently reported laser ionization mass spectrometry experiments on benzene is the extensive fragmentation of the molecules into smaller and, energetically, more costly ions, some requiring a minimum energy equivalent to nine UV photons. In most of these experiments use was made of UV[1-4, 6-8] or UV plus visible[5] laser radiation. Our results, obtained using visible laser radiation, confirmed the above feature although they showed some differences probably due to the higher laser intensity values we used in comparison to those reported in the literature. Figure 3 plots the relative abundances of various ion fragments relative to different values of laser fluence at the resonant wavelength of 4716 Å, and a benzene gas pressure of 10^{-5}. As clearly seen, the C^+ fragment is the most abundant in the whole range of laser fluences utilized, while the $C_6H_6^+$ ion is practically absent. Moreover, the C^+ ion percentage increases with increasing laser fluence,

while the $C_3H_x^+$ and $C_4H_x^+$($i=1,\ldots,6$) ion groups show an opposite behavior.

This is not the place for a thourough discussion either of the many experimental results on the unimolecular decay constant of benzene positive ions[16,17], and on branching ratios for fragmentation to different products[18,19], or of the several theories developed for explaining the dissociation dynamics of the photoion products[20]. Here we limit ourselves to quote the so-called information theoretical approach, introduced by Levine[21,22,23] (see also ref. 24), and applied in ref. (25) for calculating the distribution of parent and product-ions. An experimental test of the above theory of M.P.I. fragmentation has been described in ref. (26), while an accurate model, which considers the secondary products as produced by optically exciting the ladder of primary products, has been described by Schlag, Lin et al[27] (see also references cited therein). We carried out a further test on the factors determining the relative abundances of the six C_i ($i = 1,\ldots,6$) fragment ions by obtaining mass spectra at different wavelengths and pressures, with constant laser power. The results are summarized in Fig. 4 for two different wavelengths (4819 Å and 4716 Å), corresponding to the two peaks in the spectrum of Fig. 2, at two different pressures (2.2×10^{-4} and 2.2×10^{-5} Torr). As seen, there is little or no difference in the mass spectra, although the pressure changed by one order of magnitude. Moreover, increasing the wavelength, thus decreasing the photon energy, causes an increase in the percentage of heavier ions produced. We also checked mass spectra for other values of the gas pres-

sure in the range $10^{-4} \div 10^{-6}$ Torr, and at different wavelengths in the range of interest, obtaining similar results.

Finally, the log-log graph of figure 5 reports the dependence of total ion yield on laser power, for two resonant(4819 Å and 4716 Å), and one non-resonant (4915 Å) laser wavelengths. The straight lines were obtained by using the least square method. In the case of $\lambda = 4915$ Å the slope is 4.2 ± 0.2, which corresponds to a true (non resonant) four-photon process. On the contrary, for both resonant wavelengths the slope is 2.9 ± 0.1, thus showing a third power dependence on laser power.

It must be noted that the above values are an average between the different values characterising the "power laws" of various C_i fragments (smaller fragments are characterized by higher power dependences). However, the low indices of the "power laws" suggest that the first step, the two-photon excitation to the intermediate state, is the rate limiting step, while the overall m-photon fragmentation ($m=2 \div 9$) following the excitation is relatively rapid. This is in good agreement with the results reported in literature.

IV. LASER POWER DEPENDENCE ON MPI SIGNAL

As is well known[28], excitation to the lower vibrational levels of the benzene S_1 state leads to fluorescence with a quantum yield of ~ 0.25, which signals that most of the relaxation is by nonradiative channels. The fluorescence yield drops rapidly from the value of the lower levels until it ceases altogether around 41300 cm^{-1}. Concurrently, the vibronic level

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lifetimes decrease by at least 3 orders of magnitude. This has been explained[29] by assuming that a new channel of relaxation (channel three) opens up in addition to the fluorescence (channel one) and the intersystem crossing (channel two).

The above fact has important consequences on the power dependence of the total photo-ionization yield. We will see in the following that the relaxation rate γ for the band $14_0^1 1_0^n$ is comparable with the two-photon ionization rate $\sigma_2 I^2$ corresponding to the transition from $^1B_{2u}$ to the continuum (where σ_2 is the cross section of the process, and I the laser intensity).

In order to have a better understanding of the dependence on I of the total photo-ionization yield in our experiment we followed an approach similar to that outlined by Parker et al.[2]. In analyzing a three-photon ionization process, they used a "rate equations" approximation since the two conditions indicated by Ackerhalt et al.[30] for neglecting coherent effects in the analysis of MPI processes, were fully satisfied. First, the successive transitions from the ground state to the ion had successively increasing rates, and, second, the final step (ionization) irreversibly removed the molecule from the system. The same conditions hold true in our case.

Thus, denoting the C_6H_6 ground state ($^1A_{1g}$) population with N_0, the two-photon state ($^1B_{2u}$) population with N_1, and the number of ions formed with N (ionization continuum), we can write,

$$\frac{dN_0}{dt} = -N_0\sigma_1 I^2; \quad \frac{dN_1}{dt} = N_0\sigma_1 I^2 - N_1(\sigma_2 I^2 + \gamma); \quad \frac{dN}{dt} = N_1\sigma_2 I^2 \qquad (1)$$

Level 1 is populated by the two-photon absorption process $\sigma_1 I^2$ (where σ_1 is the relative cross section) and depopulated by a two-photon ionization process at a rate of $\sigma_2 I^2$, and by a non-radiative relaxation at a total rate γ. In the time domain of the laser pulse ($\simeq 10^{-8}$ sec) no repopulation of the ground state is considered. The laser pulse is approximated by a step function with height I between 0 and 10 ns, and zero otherwise.

The resulting ion population can then be calculated from eqs. (1). However, in the hypothesis that the ionization rate is determined by the slower rate of two-photon absorption (i.e. $\sigma_2 I^2 > \sigma_1 I^2$), and that the population of the two-photon state reaches a steady state in a time short compared to the 10 nsec laser pulse-width (conditions satisfied in our case), the photoionization rate $\Gamma(I)$ per pulse can be expressed in the form:

$$\Gamma(I) = \frac{\sigma_1\sigma_2 I^4}{\sigma_2 I^2 + \gamma} \qquad (2)$$

Implicit in the above simple rate equation treatment is the assumption that the laser linewidth ($\simeq 1$ cm^{-1}) is greater than the resonance width, or, equivalently, that each molecule sees the same field.

The TPA cross section σ_1 of benzene S_0-S_1 transition is reported to be of the order of 10^{-51} cm^{4}sec[12]. γ depends on the distance of the specific vibronic transition from the 0–0 one. It has been observed, as already said, that for bands differing more than 3000 cm^{-1} from the 0–0 origin, γ grows so much as to quench completely the TPA fluorescence. In particular, this

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condition applies to the $14_0^1 1_0^n$ band for n > 1. For γ much larger than $I^2\sigma_2$ the photoionization probability becomes proportional to the 4th power of the intensity, and the whole process can be interpreted as a non-resonant four- photon ionization. On the opposite, for $\gamma \ll I^2\sigma_2$, Γ results equal to $\sigma_1 I^2$. In this latter case, the MPI is similar to a TPA spectrum.

For intermediate cases, a more accurate evaluation of the photoionization rate is in order. In fact, what we have measured in our experiment is the total number N of photo-ions produced in a pulse of the focused laser beam. Since $\Gamma(I)$ gives the local rate of producing ions, N is given by,

$$N = nT\int_V \Gamma[I(\underline{r})]d^3r \quad , \qquad (3)$$

where T is the laser pulse duration, n is the benzene molecule concentration and V the laser-molecule interaction volume. We have indicated the dependence of I on the position $\underline{r}$ in the focal region, since its spatial variation can modify markedly the N dependence on laser fluence.

In particular, we assumed a Gaussian pattern for the focused beam,

$$I(\rho,z) = I_{max}\,\frac{\exp\{(-2\rho^2)/[w_0^2(1+z^2/z_R^2)]\}}{z^2/z_R^2 + 1}, \qquad (4)$$

w_0 being the beam waist and $z_R = \pi w_0^2/\lambda$ the Rayleigh distance. ($z_R \simeq 10^{-1}$ mm, which is much smaller than the narrow hole (2

mm) through which the photoions are pushed toward the field-free region of the TOF spectrometer).

For the sake of notational simplicity, we will use in the following the normalized distance $\zeta = z/z_R$. Now, inserting eq.(4) into eq.(2), and the resulting expression for $\Gamma(I)$ into the integral of eq. (3) one has,

$$\frac{N}{n} = 2\overset{\pi}{\ } T I^4_{max}\sigma_1\sigma_2\int_0^\infty d\zeta\int_0^\infty \rho d\rho\,\frac{\exp[(-8\rho^2)/(w_0^2(1+\zeta^2))]}{\sigma_2 I^2_{max}\exp\{(-4\rho^2)/[w_0^2(1+\zeta^2)]\} + \gamma(1+\zeta^2)^4}\ \underset{(1+\zeta^2)^2}{\ } \qquad (5)$$

Next, making the change of variable $x = \exp[-4\rho^2/w_0^2(1+\zeta^2)]$, eq. (5) reads,

$$\frac{N}{n} = 2\pi T I^2_{max}\sigma_1\frac{w_0^2}{4}\int_0^\infty d\zeta\,\frac{1}{1+\zeta^2}\int_0^1 dx\,\frac{x}{x + [\gamma(1+\zeta^2)^2]/\sigma_2 I^2_{max}} =$$

$$= 2\pi T I^2_{max}\sigma_1\frac{w_0^2}{4}\int_0^\infty d\zeta\,\frac{1}{1+\zeta^2}\left\{1 - \frac{\gamma}{\sigma_2 I^2_{max}}(1+\zeta^2)\ln\left[1 + \frac{\sigma_2 I^2_{max}}{\gamma(1+\zeta^2)^2}\right]\right\} = 2\pi T\sigma_1 I^2_{max}\frac{w_0^2}{4}F(\sigma_2 I^2_{max}/\gamma) , \qquad (6)$$

where

$$F(y) = \int_0^\infty dx \frac{1}{1+x^2}\left\{1 - \frac{(1+x^2)}{y} \ln\left[1 + \frac{y}{(1+x^2)^2}\right]\right\}$$

$$= \pi y \sum_{m=0}^{\infty} (-1)^m \frac{y^m}{m+2} \frac{(4m+4)!}{[(2m+2)!]^2} \frac{1}{2^{4m+5}} , \qquad (7)$$

where the series expansion applies for $y < 1$ only.

Now, F(y) can be calculated numerically for every given value of $y = \sigma_2 I^2_{max}/\gamma$. Thus, inserting the appropriate value of F(y) into eq. (6), one can calculate the number of ions produced per laser shot, corresponding to specific values of the laser intensity in the focus (I_{max}), of the cross section σ_2, and of the non-radiative relaxation rate .

Inversely, one can use equation (6) in order to work out the value of the ratio σ_2/γ which gives the best fit to the experimental results, at any given I_{max}. Thus, from the value of the above ratio one can get information about σ_2 or γ, depending on which of the two variables is unknown, for a specific process.

This is what we did. In fig. 6 we report the comparison between numerical (continuos line) and experimental values of the total number of ions produced (N) as a function of the laser intensity, for two different wavelengths. I is normalized to its maximum value $I_\circ$ ($I_\circ = I_{max} = 1.5\times10^{29}$ photon $cm^{-2}sec^{-1}$), and N to the corresponding $N_\circ$ value (for $\lambda = 4716$ Å). The theoretical curve of fig. 6 was obtained with the following value of the ratio σ_2/γ,

$$\frac{\sigma_2}{\gamma} = 4.10^{-58}\ cm^4 sec^2 . \qquad (8)$$

By inserting into eq.(8) the value $\gamma = 10^{11} sec^{-1}$ reported by Ref. 12 and 29 for a transition differing more than 3000 cm^{-1} from the 0–0 origin (as for $\lambda = 4716$ Å $(14^1_0 1^3_0)$, and $\lambda = 4819$ Å $(14^1_0 1^2_0)$), we infer for σ_2 the value,

$$\sigma_2 \simeq 4 \times 10^{-47}\ cm^4 .sec \qquad (9)$$

This value for the two-photon ionization cross section from the $^1B_{2u}$ state of benzene, not yet known in literature, is comparable to typical cross sections for two-photon absorption processes[13] ($\sim 10^{-50}$ $cm^4 sec$). On the contrary, it is quite different from the value estimated in ref. 12 by using identical values for γ and σ_1 ($\sigma_2 \simeq 10^{-41}$ $cm^4 sec$).

Finally, we note that the value $\sigma_2 \simeq 4 \times 10^{-47}$ $cm^4 sec$ is not too far from $\sigma_2 \simeq 4.3 \times 10^{-48}$ $cm^4 sec$, which is obtained by equating the two addends in the denominator of eq.(2). Namely they must be, of the same order of magnitude,

$$\gamma \simeq \sigma_2 I^2 , \qquad (10)$$

owing to the third power law found in our experiment (see fig. 5).

V. CONCLUSIONS

The third power law obtained for the dependence of the total

number of benzene photoions on laser intensity , at the two resonant wavelengths $\lambda = 4716$ Å and $\lambda = 4819$ Å, indicates that the photoionization rate $\sigma_2 I^2$ from the $^1B_{2u}$ excited state is comparable to the non-radiative relaxation rate γ for these transitions. In this case, a more accurate evaluation of the photoionization rate is necessary. By carrying out this analysis, we have outlined a simple method which allows one to work out a value for the ratio σ_2/γ by fitting the experimental results. From the obtained value of the above ratio, one can get information about σ_2 or γ, depending on which of the two variables is unknown. By applying this method we have inferred the value $\simeq 4 \times 10^{-47}$ $cm^4 sec$ for the two-photon ionization cross-section from the $^1B_{2u}$ excited state of Benzene at $\lambda = 4716$ Å and $\lambda = 4819$ Å.

Our method is more generally applicable to other processes where the same conditions of our experiment are satisfied.

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FIGURE CAPTIONS

FIG. 1 - Experimental set-up (see text for a full description).

FIG. 2 - Normalized MPI spectrum of benzene.

FIG. 3 - Relative abundances of various ion fragments at the resonant wavelength of 4716 Å, for different fluences.

FIG. 4 - Relative abundances of various ion fragments for p = 2.2×10^{-4} Torr, and p = 2.2×10^{-5} Torr, at two different wavelengths ($\lambda = 4716$ Å white area, $\lambda = 4819$ A dashed area)

FIG. 5 - Log-log plot of the dependence of total ion yield on laser power for two resonant (4716 Å and 4819 Å) and one non-resonant (4915 Å) wavelengths.

FIG. 6 - Comparison between theoretical (continuos line) and experimental values of the total number of ions produced as a function of the laser intensity for two different wavelengths ($I_\circ$ is the maximum value of laser intensity, and $N_\circ$ the corresponding value of N, for $\lambda = 4716$ Å).

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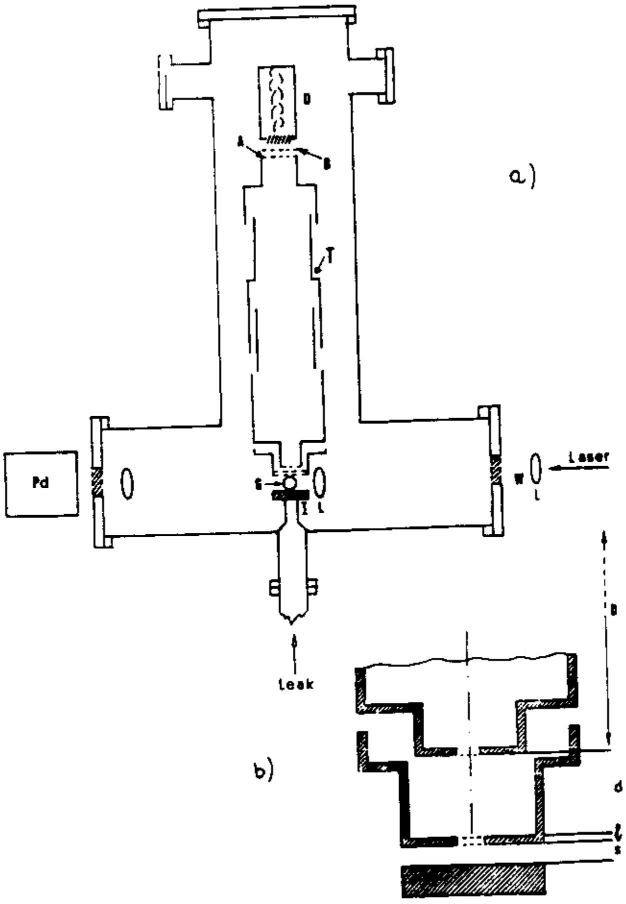

FIG.1

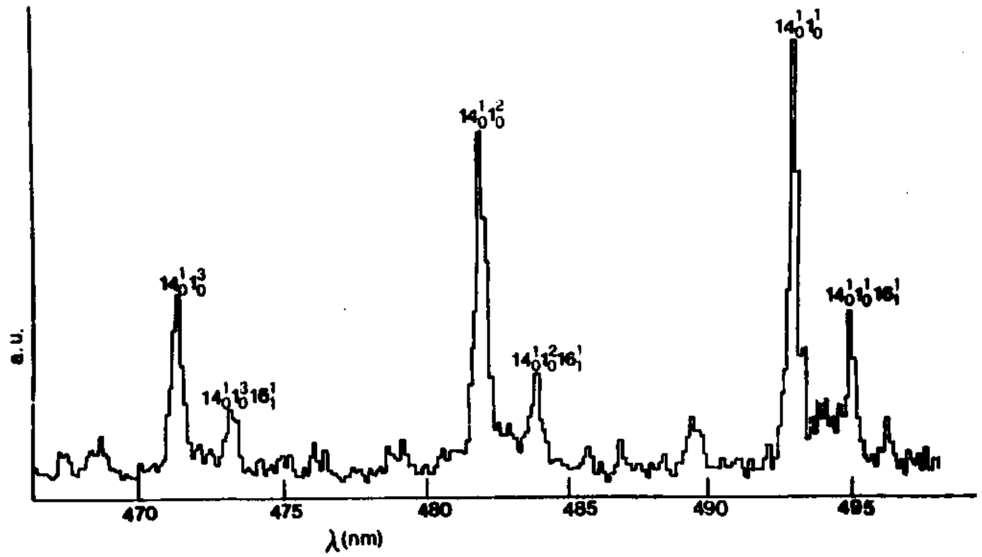

FIG.2

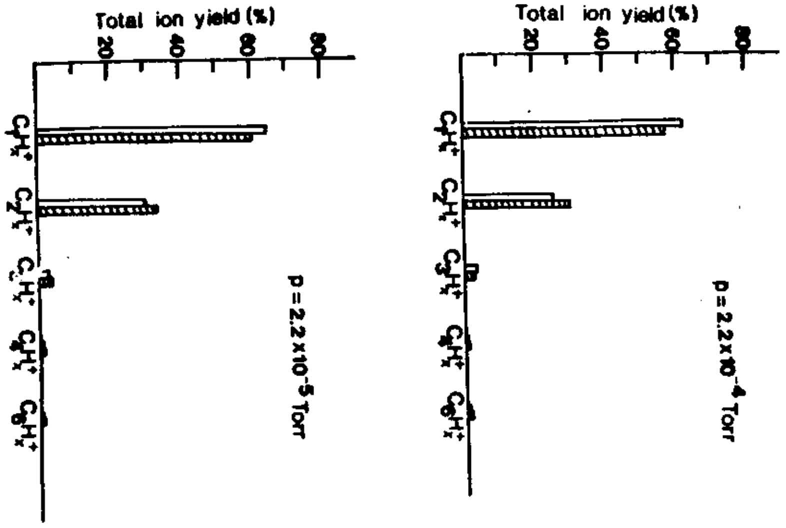

FIG.4

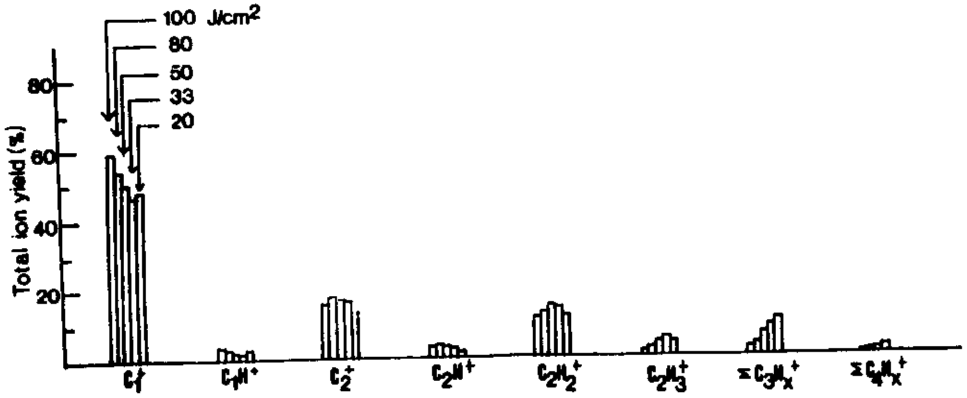

FIG.3

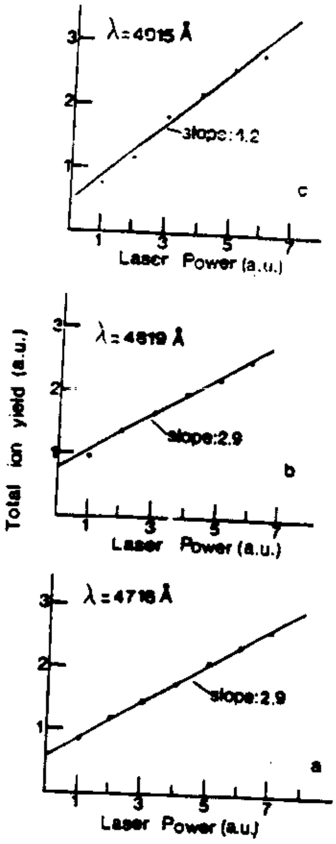

FIG.5

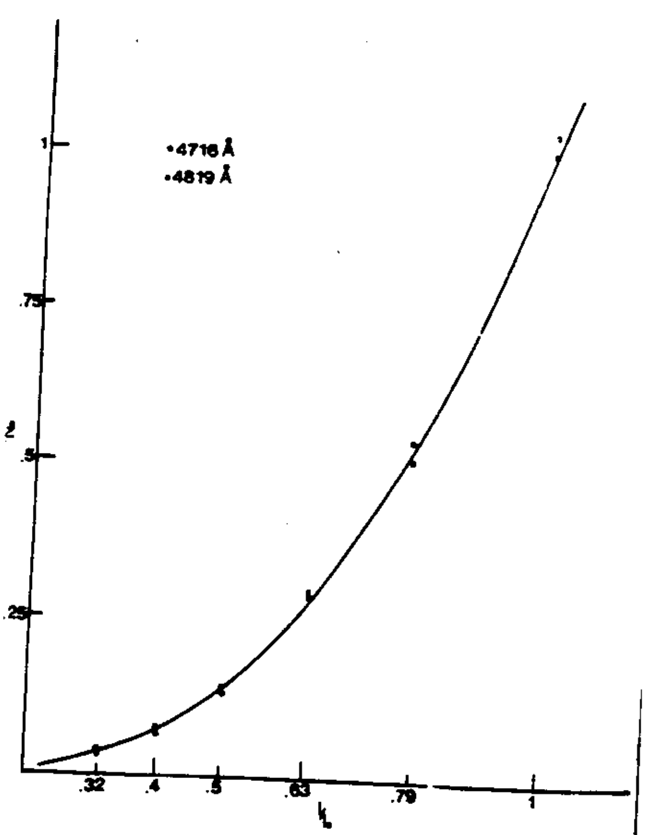

FIG.6

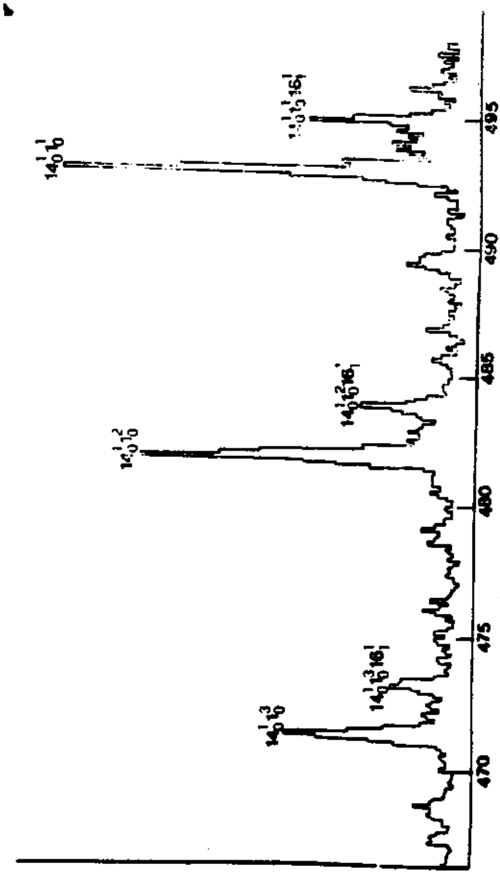

FIG.2

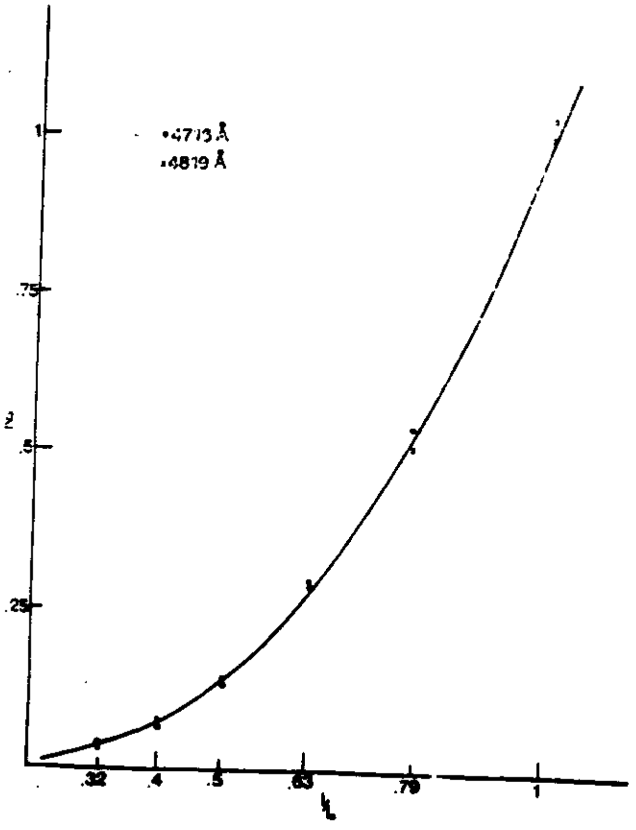

FIG.6