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Multiphoton ionization of molecular nitrogen by a neodymium-glass laser

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Multiphoton ionization of molecular nitrogen N_2 is investigated by using a neodymium-glass laser. The atomic ions N^+ and the molecular ions N_2^+ produced during the interaction are separated by a time-of-flight analyzer and collected on the cathode of an ion multiplier. The experimental results give the values 9 ± 1 for the nonlinear interaction order for N_2^+ and 12 ± 1 for N^+, and then lead to the determination of separate probabilities of multiphoton formation of N_2^+ and N^+; for a flux value of 2.44×10^{12} W/cm^2, these probabilities are, respectively, $3\times10^{6\pm0.7}$ sec^{-1} and $2\times10^{7\pm0.7}$ sec^{-1}. The multiphoton excitation, ionization, and dissociation processes of N_2 are discussed.

I. INTRODUCTION

Multiphoton ionization (MPI) of atoms by laser radiation has been actively investigated during the last ten years.[1] The description of the interaction of laser radiation with molecules is also of interest and numerous works, both theoretical[2] and experimental,[3] are nowadays devoted to MPI of molecules.

Multiphoton processes induced by infrared laser radiation in a molecule are complicated in comparison with the analogous problems in an atom by the necessity of taking into account a great number of eventual intermediate resonant states (vibrational and rotational). Experimental analysis of MPI of molecules is additionally complicated by the fact that ionization of molecules can result in molecular or atomic ions which arise from dissociation of excited neutral molecules or excited molecular ions.

So, for the experimentation, various techniques such as optical spectroscopy, collection and detection of fragment ions by magnetic mass spectrometer, or time-of-flight mass spectrometer are necessary to clarify the different absorption processes and their relative importances.

The multiphoton collisionless processes in molecules were established and studied experimentally for the first time during research on the interaction between the radiation of Nd laser (and its second harmonic) and some diatomic molecules, especially hydrogen molecule.[4,5] The interaction of H_2 with a ruby laser was studied by Voronov *et al.*,[6] and with a CO_2 laser by Ambartzumian *et al.*[7]

We have chosen the nitrogen molecule for experimental studies because it has been relatively well investigated and has well-known potential energy curves.

We have been in search of coincidences between the added energy of some quanta of laser radiation and the energy of a molecular transition. Moreover, we have to take into account the selection rules extended to multiphoton transitions and the Franck-Condon factors relative to these transitions. This suggests to us the various multiphoton processes leading to the dissociation of N_2 and the ionization of N_2 and N.

In a previous letter[8] we presented the results of an experiment on MPI of N_2 at low pressure (10^{-3} Torr) by neodymium-laser radiation. The experiment consisted essentially by measuring the total number of ions produced during the interaction, without discrimination between atomic and molecular ions, as a function of laser intensity. We found a nonlinear interaction order of 13 ± 2 and proposed some reactions to explain the results.

In one other paper[9] we reported the results of an experiment which used an optical spectroscopy diagnostic for the MPI of N_2 by the Nd-laser radiation. This experiment showed the presence of the two ion species, N_2^+ and N^+ in the interaction volume, and was performed at a gas pressure less than about 2 Torr which was the minimum pressure value compatible with the sensitivity of the used experimental detection system. At pressures greater than 10^{-2} Torr, there are two mechanisms that can lead to the ionization of a gas when irradiated with a high-intensity laser beam, the multiphoton process, and a cascade- or collision-induced absorption. For nitrogen, at about 2 Torr we showed that the multiphoton absorption dominates

over the cascade mechanism. From the analysis of the light emitted by some excited states of N_2 and N, we presented various absorption processes which lead to the ionization and the dissociation of N_2 and to the ionization of N.

Starting from these previous qualitative results, we present now an experiment which gives more details on the understanding of the MPI of N_2 and permits us the determination of the probabilities of MPI for N_2^+ and N^+ by a Nd-laser radiation.

The ions liberated by multiphoton absorption in the gas are directed to the first dynode of an ion multiplier and amplifying system. Ion species identification is effected by time-of-flight analyzer. The number of ions N_2^+ and N^+ is measured.

II. EXPERIMENT AND RESULTS

A. Experimental arrangement

The radiation source used is a Nd-glass laser Q switched by a rotating prism. The light beam is linearly polarized. The laser pulse duration is about 30 nsec (FWHM), and the energy per pulse is about 5 J distributed over some hundred modes. The spectral profile of the radiation centered on 10 600 Å is Gaussian with a bandwidth of about 30 Å (FWHM). The laser beam is focused with a spheroparabolic lens of $f=6$ cm focal length into the interaction chamber. For the lens used, the diameter of the focus spot is limited by the divergence θ of the laser beam which is measured equal to 1.375×10^{-3} rad. The focused spot diameter is inferred from θ and is $d=f\theta=8.25\times10^{-3}$ cm. The interaction volume is cylindrical and its length is given by[10]

$$l=2(\sqrt{2}-1)f^2\theta/D\ ,$$

where D is the unfocused beam diameter $D=15$ mm and then $l=2.73\times10^{-2}$ cm.

The maximum intensity of the laser flux is about 3×10^{12} W/cm^2 (1.6×10^{31} photons sec^{-1} cm^{-2}) in the focus region. The incident radiation intensity is varied by means of neutral density filters interposed in the beam. A part of the incident light is reflected onto a photodiode (ITT FW114A) with a rise time less than 10^{-9} sec. The output current of the photodiode is recorded on one channel of a dual-beam oscilloscope (Tektronix 7844).

This measurement system is previously calibrated with a calorimeter and allows us to know the instantaneous laser intensity incoming in the interaction chamber. The nitrogen gas is injected in the vicinity of the focus point, perpendicularly both to the axis of detection and to the axis of the beam. Because of the low pressure used $p_0=4\times10^{-4}$ Torr which corresponds to a density of neutral nitrogen molecules $n_0=1.416\times10^{13}$ cm^{-3}, a continuous flow of gas is established in order to limit the presence of impurities desorbed by the walls in the interaction region.

The ions created during the interaction are accelerated by a dc electric field, separated by a time-of-flight spectrometer, and collected on the cathode of an ion multiplier (RTC 50 P 3R), the output current of which is measured on the second channel of the oscilloscope.

For an increase in energy of the ions of about 1500 eV and a distance of flight of some cm, the time separation between the collection of the N^+ ions and the N_2^+ ions is about 10^{-7} sec. A schematic drawn of the experimental arrangement is given in Fig. 1.

B. Experimental results

In Fig. 2 we show typical oscillograms of the collection signals (upper trace) for three different laser intensities (lower trace). In the upper trace, the first peak located on the left side corresponds to the detection of the N^+ ions and, separated by about 200 nsec, the peak corresponding to the detection of the N_2^+ ions. It is worthy of note that the number of parasitic ions due to MPI of impurities in the residual pressure is negligibly small.

Figure 3 shows the number of ions N_2^+ and N^+ collected after the interaction versus the peak laser intensity ϕ_0. These numbers are proportional to ϕ_0^K, where the two values of K are defined as

$$K_1=d\log_{10}[N_2^+]/d\log_{10}\phi_0$$

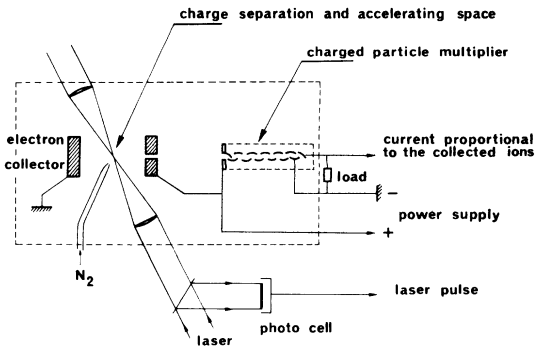

FIG. 1. Experimental setup.

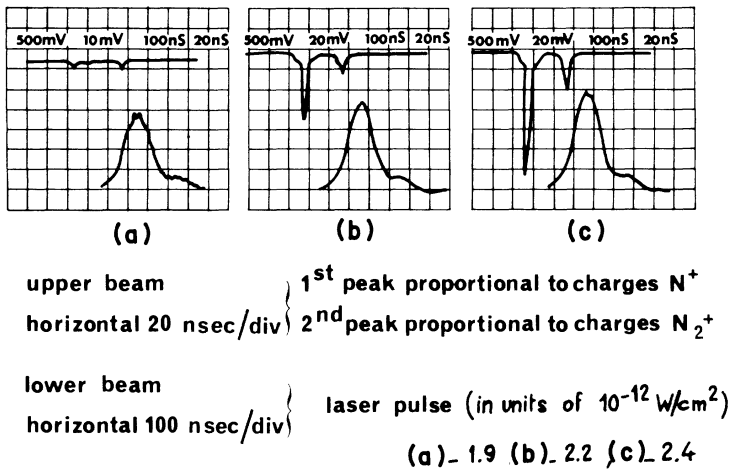

FIG. 2. Set of oscillograms of signals detected (upper traces) for three increasing laser intensities (lower traces).

and

$$K_2 = d \log_{10}[N^+]/d \log_{10}\phi_0 .$$

We find that for $\phi_0 \leq 2.44\times 10^{12}$ W/cm^2, $K_1 = 9\pm 1$, and $K_2 = 12\pm 1$. For $\phi_0 = 2.44\times 10^{12}$ W/cm^2 the numbers of collected ions are $[N_2^+] = 1.3\times 10^5$ and $[N^+] = 4.94\times 10^5$.

C. Determination of the MPI probabilities

From the multiphoton theory the number of molecular ions formed $d[N_2^+]$ during a time interval dt in a volume dv is given by

$$d[N_2^+] = n_0 W(N_2^+) dv\, dt , \quad (1)$$

where n_0 is the density of neutral nitrogen molecules and $W(N_2^+)$ is the probability of multiphoton creation of molecular ions.

We write an analogous relation for atomic ions $d[N^+]$ with a probability $W(N^+)$:

$$d[N^+] = n_0 W(N^+) dv\, dt . \quad (2)$$

Formally the MPI probability is expressed by $W = \sigma_K \phi^K K!$, where σ_K is the MPI "cross section," ϕ the laser flux, K the nonlinear order, and the factor $K!$ (K-order correlation function) is due to the fact that the laser used is multimode. The probabilities $W(N_2^+)$ and $W(N^+)$ can be expressed in the form

$$W(N_2^+) = \sigma_9^{(M)} \phi^9 9! \quad (3)$$

and

$$W(N^+) = \sigma_{12}^{(A)} \phi^{12} 12! , \quad (4)$$

where $\sigma_9^{(M)}$ and $\sigma_{12}^{(A)}$ are the MPI cross sections for N_2^+ and N^+, respectively.

It has been shown[11] that when the laser radiation contains numerous oscillating modes (greater than 10^2), the $K!$ factors are to be included in the expression of the probability of multiphoton absorption to enhance the rate of MPI as compared to a coherent radiation field. This is the case in the experiment reported here, where the spectrum of the Nd-glass laser radiation contains approximately 10^3 independently oscillating axial modes. More recently Dixit and Lambropoulos[12] have shown that if the photon frequency—or a multiple of it—is in resonance with intermediate bound states, the enhancement of probability of MPI can be larger than $K!$, but depends on the details of the processes and the intensity of the laser field. In this experiment, although two or several near-resonant intermediate states are possible, this enhancement factor is yet kept equal to $K!$ the average number of photons being small in each laser mode.

The total numbers of ions $[N_2^+]$ and $[N^+]$ per laser pulse are given by

$$[N_2^+] = n_0 9! \sigma_9^{(M)} \int\int \phi^9 dv\, dt \quad (5)$$

and

$$[N^+] = n_0 12! \sigma_{12}^{(A)} \int\int \phi^{12} dv\, dt . \quad (6)$$

For the laser used, the radial distribution in the focal plane and the temporal evolution of the flux can be assimilated to Gaussian distributions; then the laser flux is expressed as

$$\phi = \phi_0 \exp\left[-\left[\frac{t}{\tau}\right]^2\right] \exp\left[-\left[\frac{r}{r_0}\right]^2\right] , \quad (7)$$

where τ is the laser-pulse duration $\simeq 30$ nsec and

$$r_0 = f\theta/2 = 4.125 \times 10^{-3} \text{ cm}.$$

In MPI processes it is convenient to define[13] for a Kth-order process an "effective" interaction time

$$\tau_K = \int_{-\infty}^{+\infty} \exp(-Kt^2/\tau^2)dt = (\pi/K)^{1/2}\tau$$

which gives, in our case, $\tau_9 = 17.7$ nsec and $\tau_{12} = 15.35$ nsec, and an effective interaction volume

$$V_K = 2\pi l \int_0^{\infty} r \exp(-Kr^2/r_0^2)dr = \pi l r_0^2/K = V_0/K \ ,$$

where $V_0 = \pi r_0^2 l$ is the actual interaction volume with l previously defined is equal to 2.73×10^{-2} cm, which gives $V_9 = 1.62 \times 10^{-7}$ cm^3 and $V_{12} = 1.22 \times 10^{-7}$ cm^3.

Finally we find the multiphoton probabilities at $\phi_0 = 2.44 \times 10^{12}$ W/cm^2:

$$W(N_2^+) = \frac{[N_2^+]}{n_0 V_9 \tau_9} = 3.19 \times 10^6 \tag{8}$$

and

$$W(N^+) = \frac{[N^+]}{n_0 V_{12} \tau_{12}} = 1.87 \times 10^7 \tag{9}$$

in units of sec^{-1}. We deduce the MPI cross section $\sigma_9^{(M)}$ and $\sigma_{12}^{(A)}$:

$$\sigma_9^{(M)} = \frac{W(N_2^+)}{9!\phi_0^9} = 2.87 \times 10^{-111} \text{ W}^{-9}\text{cm}^{18}\text{sec}^{-1} \tag{10}$$

and

$$\sigma_{12}^{(A)} = \frac{W(N^+)}{12!\phi_0^{12}} = 8.72 \times 10^{-151} \text{ W}^{-12}\text{cm}^{24}\text{sec}^{-1} \ . \tag{11}$$

Analysis of experimental data shows that the ionization probabilities W are subject to an uncertainty of $\Delta \log_{10} W \simeq 1$, due to uncertainties in the values of n_0, V_K, τ_K, $[N_2^+]$, $[N^+]$, and ϕ_0. The values of W are then to be given in the form

$$W(N_2^+) \simeq 3 \times 10^{6\pm 1} \text{ sec}^{-1}$$

and

$$W(N^+) \simeq 2 \times 10^{7\pm 1} \text{ sec}^{-1} \ .$$

Let us remark that the discontinuities in the slopes in Fig. 3 which are usually attributed to the ionization of all the molecules present in the interaction zone would lead to values of $[N_2^+]$ and

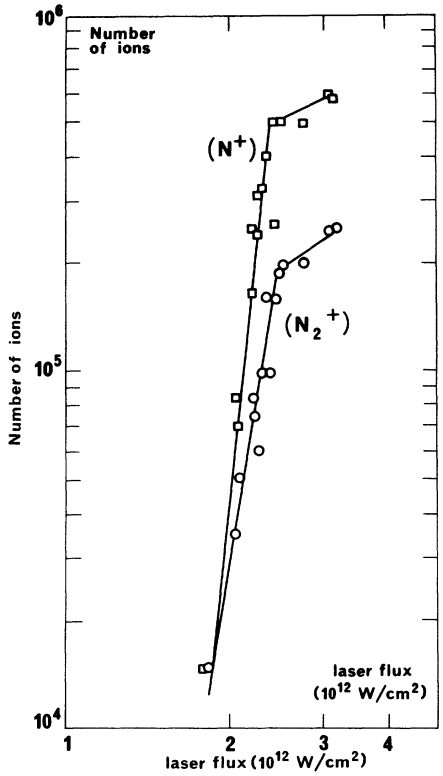

FIG. 3. Number of ions N_2^+ and N^+ collected versus the peak laser intensity ϕ_0.

$[N^+]$ greater than those obtained by direct measurements. A calculation of the trajectories of the ionized particles taking into account the values of the dc accelerator field and the dimension of the hole of the collector, shows therefore that all the ions produced in the interaction volume are collected and measured. Moreover, the time-of-flight is short enough to neglect ion loss. More precisely, if we consider an interaction volume value of about 1.5×10^{-7} cm^3 the number of molecules is $[N_2] = n_0 V_K = 2.13 \times 10^6$. The experiment shows that at the flux $\phi_0 = 2.44 \times 10^{12}$ W/cm^2, the number $[N^+]$ is about four times greater than the number $[N_2^+]$; we can write

$$[N_2] = [N_2^+] + \tfrac{1}{2}[N^+] \simeq 3[N_2^+]$$

which leads to the values $[N_2^+] \simeq 7.1 \times 10^5$ and $[N^+] = 2.84 \times 10^6$ instead of 1.3×10^5 and 4.9×10^5, respectively. Nevertheless, the probability values are, in the case where depletion is occurring,

$$W(N_2^+) \simeq 1.5 \times 10^7 \text{ sec}^{-1}$$

and (12)

$$W(N^+) \simeq 10^8 \text{ sec}^{-1} \ .$$

These values are in the range of those mentioned above.

The main uncertainty in the determination of the probabilities by using the discontinuities in the slope is connected with the fact that the curves $\log[N_2^+]$ or $\log[N^+]$ versus $\log\phi_0$ reach saturation over a finite range of intensities. Strictly speaking the slopes must vary continuously from 9 (or 12) to values of the order of unity. This is due to the nonuniform distribution of the field in the interaction volume and to the spread of the signal due to laser instability. From our point of view, we think that, at $\phi_0 \simeq 2.44\times10^{12}$ W/cm^2, the depletion is achieved only in the central part of the interaction zone but not in the whole focus volume; the MPI phenomenon is not straightway entirely masked. It is obvious that, for ϕ_0 values greater than 2.44×10^{12} W/cm^2, the depletion governs the processes.

Moreover, the W values obtained in (12) which assume the total depletion are the limit possible values for W. Consequently, the uncertainties given above can be limited to $\Delta\log_{10}W\simeq0.7$ instead of $\Delta\log_{10}W\simeq1$. In these conditions it would seem reasonable to give the values $W(N_2^+)$ and $W(N^+)$ in the form $W(N_2^+)=3\times10^{6\pm0.7}$ sec^{-1} and $W(N^+)=2\times10^{7\pm0.7}$ sec^{-1}.

III. DISCUSSION

It should be interesting, to justify our results, to analyze in more detail the successive processes of multiphoton absorption which lead to the observed ions N_2^+ and N^+. One approach is to consider the experimental values found for the order of interaction 9 ± 1 and 12 ± 1 and to research all the multiphoton resonances with the aid of the potential energy curves of N_2, N_2^+, N, and N^+. Resonances appear when the energy of transitions from an initial state to some electronic, vibrational, or rotational level coincides with the energy of an integer number of quanta and when the selection rules for a K-photon transition derived by successive applications of selection rules for one-photon processes are not violated. In this discussion, we do not take account of the displacement effects and broadening effects of the atomic or molecular levels under the influence of the electric field of the laser beam. We assume that they are small enough to be neglected compared to the width of the K-order laser radiation. Moreover, due to the great number of rotational levels, we may suppose that the multiphoton resonances are not destroyed during the interactions and that no other resonances are created. In this discussion we have to account for the fact that the probability of production of N^+ is greater than that of N_2^+. It seems also interesting to try to understand the origin of the atomic nitrogen ions N^+ resulting mainly from dissociation of either N_2 or N_2^+.

A. Selection rules

The selection rules, used in this discussion, for laser-induced molecular transitions, are deduced from the data given by Herzberg, Lau, and Bunkin.[14] The selection rules for K-photon transitions are those obtained by K successive single-photon transitions and they may be expressed as follows.

(a) The fact that the Franck-Condon principle which stipulates that multiphoton transitions occur with no change in the internuclear distance at the moment of the electron jump and no change of the velocity.

(b) The fact that the spin conservation $\Delta S=0$ which states that terms of different multiplicities cannot combine with one another.

(c) In the case of a molecule with nuclei of equal equal charge, we have the rule that, for K even, only $g\leftrightarrow g$ and $u\leftrightarrow u$ transitions are allowed, and for K odd, only $g\leftrightarrow u$ transitions are allowed.

(d) The selection rules[15] on the electronic quantum number Λ and on the quantum number of the total angular momentum J are not yet explicitly expressed for a K-photon transition with $K>2$. We are concerned in this discussion by the rotational quantum number J instead of the quantum number K because we study states for which $S=0$. For a one-photon transition, the selection rules are $\Delta\Lambda=0,\pm1$ and $\Delta J=0,\pm1$. It results that the selection rules for a K-photon transition between two bound states are given by $\Delta\Lambda=0,\ \pm1,\ \pm2,\ \ldots,\ \pm K$ and, for a given electron term, $\Delta J=0,\pm1,\pm2,\ \ldots,\ \pm K$. It should be thought that the smaller $|\Delta J|$, the greater the probability for a K-photon transition. These selection rules are summarized in Table I.

B. Multiphoton transitions from the ground state $X\,^1\Sigma_g^+$

The population of the vibrational levels of the N_2 electronic ground state is described by the Boltzmann distribution and the ratio of the number of molecules in the first to that in the zeroth

TABLE I. Selection rules.

K order	Multiplicity	Symmetry	Electronic quantum number	Total quantum number
even	$\Delta S=0$	$g \leftrightarrow g$ $u \leftrightarrow u$ $g \not\leftrightarrow u$	$\Delta\Lambda=0,\pm1,\ldots,\pm K$	$\Delta J=0,\pm1,\ldots,\pm K$
odd	$\Delta S=0$	$g \leftrightarrow u$ $g \not\leftrightarrow g$ $u \not\leftrightarrow u$	$\Delta\Lambda=0,\pm1,\ldots,\pm K$	$\Delta J=0,\pm1,\ldots,\pm K$

vibrational state is equal to 1.4×10^{-5} for 300 K. The contribution of the levels with $v\geq1$ is thus quite negligible and all the transitions have $v=0$ in the initial state.

The number of molecules N_J in the rotational level J of the lowest vibrational state $X\,^1\Sigma_g^+$ $(v=0)$ is given by

$$N_J\simeq(2J+1)\exp[-2J(J+1)/(2J_M+1)^2]\,, \tag{13}$$

where J_M is the value of J for which N_J goes through a maximum. $J_M\simeq0.6\sqrt{T/B}-0.5\simeq6.7$ for $T=300$ K, where the rotational constant B is equal to about 2 cm^{-1}. From the relation (13) we deduce that the populations of the rotational states which have J values between 2 and 13 are greater than $N_{J_M}/2$. We shall now confine our discussion on these most populated levels which represent the major part ($\geq80\%$) of the population of the ground state.

There is a K-photon resonance when the energy of transition from the initial $X\,^1\Sigma_g^+$ $(v=0,2\leq J\leq13)$ to some vibrational-rotational level of another electronic state coincides with the energy of K photons. The research of such multiphoton resonances has to take into account the fact that the resulting intensity profile of the K-photon laser radiation is Gaussian with FWHM equal to $\Gamma\sqrt{K}$, where $\Gamma=27$ cm^{-1} is the width of the laser radiation, and the fact that the energy of the initial state of $X\,^1\Sigma_g^+(v=0)$ is included in the range 12 $cm^{-1}-364$ cm^{-1} corresponding to $J=2$ and $J=13$, respectively.

In Fig. 4 we have indicated the most important electronic states where the potential energy is expressed both in eV and in number of photons. The examination of this figure shows that the number K of photons which can excite the ground level $X\,^1\Sigma_g^+$ is greater than seven because, on one hand, transitions between vibrational levels of the same electronic state are forbidden for the homopolar N_2 molecule and, on the other hand, the lowest $A\,^3\Sigma_u^+$, $B\,^3\Pi_g$, $W\,^3\Delta_u$ states which have spin value equal to one cannot combine with the ground state $X\,^1\Sigma_g^+$ owing to the fact that the multiplicities of the two combining states must be the same. By using the numerical data given by Lofthus and Krupenie[16] it is found that there are three values of the number

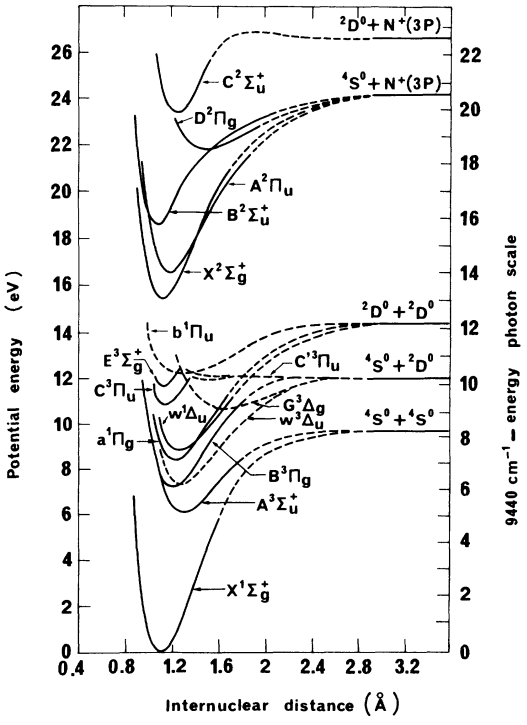

FIG. 4. Simplified potential energy curves of N_2.

K ($K=8$, 9, and 11) compatible with the selection rules which lead to transitions in which the Franck-Condon principle is satisfied. Transitions from $X\,^1\Sigma_g^+$ concerned with the absorption of 12 photons towards levels of the Rydberg series $c\,^1\Pi_u$, $o\,^1\Pi_u$, $b\,^1\Sigma_u^+$, and $c'\,^1\Sigma_u^+$ which are all ungerade, cannot take place.

In this discussion we shall not take into account the Λ-type doubling of states with $\Lambda\neq 0$ because the energy separation between the two components of each J value is very small ($<<1$ cm^{-1}).

1. *Absorption of eight photons*

The simultaneous absorption of eight photons corresponds to an energy jump of

$$8h\nu\pm(\Gamma/2)\sqrt{8}=75\,520\ \text{cm}^{-1}\pm 38\ \text{cm}^{-1}\ .$$

For the initial ($X\,^1\Sigma_g^+, v=0,2\leq J\leq 13$) levels the final energy range is 75 494 cm^{-1} – 75 922 cm^{-1}; the ($a\,^1\Pi_g, v'=4,5\leq J'\leq 17$) levels for which the energies are in the range 75 496 cm^{-1} – 75 920 cm^{-1} are resonant. The reaction is

$$N_2\,(X\,^1\Sigma_g^+, v=0,2\leq J\leq 13)+8h\nu \rightarrow N_2(a\,^1\pi_g, v'=4,5\leq J'\leq 17)\ . \qquad (14)$$

More precisely a level J of $X\,^1\Sigma_g^+$ can combine with a level J' of $a\,^1\Pi_g$ if the rule $\Delta J = J'-J=0,\pm 1,\ldots,\pm 8$ is satisfied and if the energy $E_{J'}$ of the J' level verifies the condition $E_{J'}-E_J=8h\nu\pm 38$ cm^{-1}. (ΔJ is defined afterwards as the difference between the final rotational number J', and the initial number J, E_J is the energy of the J level.) For instance, starting from the N_2 ($X\,^1\Sigma_g^+, v=0, J=4$) level, which corresponds to an energy value equal to $J(J+1)B_v\simeq 40$ cm^{-1}, the absorption of $8h\nu$ leads to an energy-range value equal to 75 522 cm^{-1} – 75 598 cm^{-1}. The energy values of the ($a\,^1\Pi_g, v'=4, J'=7,8,9$) levels given by $T_0+J'(J'+1)B_v'$, with $T_0=75450$ cm^{-1} and $B_v'=1.5356$ cm^{-1} are, respectively, equal to 75 536 cm^{-1}, 75 561 cm^{-1}, and 75 588 cm^{-1}, so that the $J'=7$, 8, and 9 levels are each coupled with the $J=4$ level of ($X\,^1\Sigma_g^+, v=0$). We thus find that the $J=2$ level of $X\,^1\Sigma_g^+$ is coupled with the levels $J'=5,6,7,8$ of $a\,^1\Pi_g$, the levels $2<J\leq 6$ are each coupled with three J' levels, with $\Delta J=3$, 4, and 5, and the levels $6<J\leq 13$ are each coupled with two J' levels, with $\Delta J=3$ and 4. Figure 5 shows an example of such a coupling.

The ($X\,^1\Sigma_g^+, v=0$)→($a\,^1\Pi_g, v'=4$) transition for which the Franck-Condon factor (FCF) is equal to 0.16 (Ref. 16) takes place with a relatively great probability.

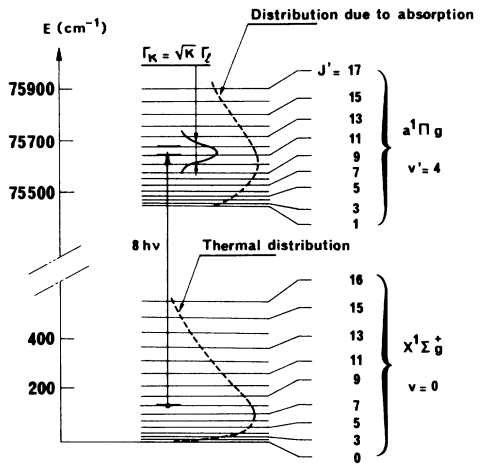

FIG. 5. Eight-photon transitions between the states $X\,^1\Sigma_g^+, v=0$ and the states $a\,^1\Pi_g$, $v'=4$. As an example, the coupling between $J=8$ and $J'=11$ and 12 is represented.

2. *Absorption of nine photons*

The energy jump corresponding to the absorption of $9h\nu$ is equal to 84 960 cm$^{-1}\pm 40$ cm^{-1}. The energy range covered is 84 932 cm^{-1} – 85 364 cm^{-1}. It is found that the allowed transitions take place from the $X\,^1\Sigma_g^+$ state into the ($w\,^1\Delta_u, v'=9,14\leq J'\leq 22$) states. Then the energy range of the ($w\,^1\Delta_u, v>6$) levels are not tabulated and are deduced by using the relation

$$\sigma_H\simeq 70\,964+1559(v'+\tfrac{1}{2})-11.6(v'+\tfrac{1}{2})^2\ , \qquad (15)$$

which gives the energy values of the heads of the bands in cm^{-1}.[16] For $v'=9$, the value $T_0=84\,683$ cm^{-1} is found by taking into account an extrapolated correction term equal to about 44 cm^{-1}. The rotational constant $B'_{v'=9}$, also extrapolated from the known values until $v'=6$, is found equal to about 1.35 cm^{-1}.

Roughly speaking the reaction is

$$N_2(X\,^1\Sigma_g^+, v=0,2\leq J\leq 13)+9h\nu \rightarrow N_2(w\,^1\Delta_u, v'=9,15\leq J'\leq 22)\ . \qquad (16)$$

Strictly speaking the levels $2\leq J\leq 5$ of $X\,^1\Sigma_g^+$ are not coupled with J' levels because $\Delta J>9$. For the same reason the level ($w\,^1\Delta_u, v'=9, J'=14$) which

has an energy value equal to 84 966 cm^{-1} included in the interaction energy range is not yet coupled. The levels $J=6,7,8,9$ are, respectively, coupled with the levels $J'=15,16,17,18$, with $\Delta J=9$. Each of the levels $J=10,11,12,13$ are, respectively, coupled with two J' levels with $18\leq J'\leq 22$ such as $\Delta J=8$ and 9.

The Franck-Condon factors are not tabulated for the $X\,^1\Sigma_g^+\rightarrow w\,^1\Delta_u$ transitions and for the following transitions used in this study. We have therefore calculated approximate values of the FCF$=|\int\psi\psi' dr|^2$ by using vibrational eigenfunctions ψ and ψ' of the upper and lower states of the harmonic oscillator. We find a FCF$\simeq$0.09 for the $X\,^1\Sigma_g^+\rightarrow w\,^1\Delta_u$ transition, which means that this transition may occur with a relatively large probability.

3. *Absorption of eleven photons*

The absorption of eleven photons corresponds to an energy range equal to 103 807 $cm^{-1}-104\,249$ cm^{-1} and there is a resonance with the $(b\,^1\Pi_u, v'=4, 9\leq J'\leq 19)$ levels, the energy range of which is 103 816 $cm^{-1}-104\,228$ cm^{-1}. The reaction is

$$N_2\,(X\,^1\Sigma_g^+, v=0,2\leq J\leq 13)+11h\nu \rightarrow N_2(b\,^1\Pi_u, v'=4, 9\leq J'\leq 19)\ . \quad (17)$$

We find that the level $J=2$ is coupled with three levels $J'=9,10,11$, the levels $J=3$ and 4 are each coupled with $J'=10,11,12$, and $J=5$ and 6 are each coupled with $J'=11,12,13$. The levels $J=7$ and 8 are coupled with three J' levels verifying $\Delta J=5,6,7$, and the levels $9\leq J\leq 13$ are each coupled with two J' levels verifying $\Delta J=5$ and 6. The calculated value of the FCF is 0.25.

C. Transitions between two excited states of N_2

We discuss now the occurrence of the one-photon transition and the three-photon transition from the $a\,^1\Pi_g$ state to reach, respectively, the $w\,^1\Delta_u$ and the $b\,^1\Pi_u$ states and the two-photon transition from the $w\,^1\Delta_u$ state to the $b\,^1\Pi_u$ state.

1. *Excitation of the $a\,^1\Pi_g$ state*

The reaction $a\,^1\Pi_g+h\nu\rightarrow w\,^1\Delta_u$ is forbidden because the selection rule relative to the number $J, \Delta J=0,\pm 1$ is not respected for transitions which may occur from the excited $(a\,^1\Pi_g, v=4, 5\leq J\leq 17)$ levels resulting from the reaction (14). It is worthy of note that when we bring the selection rules into play, although the two reactions $X\,^1\Sigma_g^+ + 8h\nu\rightarrow a\,^1\Pi_g$ and $X\,^1\Sigma_g^+ + 9h\nu\rightarrow w\,^1\Delta_u$ can take place, the reaction $a\,^1\Pi_g + h\nu\rightarrow w\,^1\Delta_u$ cannot occur.

The reaction $a\,^1\Pi_g+3h\nu\rightarrow b\,^1\Pi_u$ takes place with a relatively high probability. In fact, it is found that the $5\leq J\leq 12$ levels of the $(a\,^1\Pi_g, v=4)$ state are, respectively, coupled with the $8\leq J'\leq 15$ levels of the $(b\,^1\Pi_u, v'=4)$ state, with $\Delta J=J'-J=3$ and the $13\leq J\leq 17$ levels are, respectively, coupled with the $15\leq J'\leq 19$ levels with $\Delta J=2$. That is,

$$(a\,^1\Pi_g, v=4, 5\leq J\leq 17)+3h\nu \rightarrow (b\,^1\Pi_u, v'=4, 8\leq J'\leq 19)\ . \quad (18)$$

The value of the FCF is found equal to about 0.02. Although this value is much smaller than that of the direct transition $X\,^1\Sigma_g^+\rightarrow b\,^1\Pi_u$ [reaction (17)] which is equal to about 0.25, one can think that the direct transition corresponding to the absorption of eleven photons is much less probable than the two-step transition $X\,^1\Sigma_g^+ + 8h\nu\rightarrow a\,^1\Pi_g$ followed by $a\,^1\Pi_g+3h\nu\rightarrow b\,^1\Pi_u$. It is inferred that the probability to obtain the $(b\,^1\Pi_u, v'=4)$ state is essentially governed by the eight-photon process. In the lack of theoretical results concerning this question we think that the three-photon excitation of the $a\,^1\Pi_g$ state occurs with a great probability as compared to the other processes. We shall consequently consider that the excitation of the $b\,^1\Pi_u$ state mainly occurs via the intermediate $a\,^1\Pi_g$ state.

2. *Excitation of the $w\,^1\Delta_u$ state*

The reaction

$$(w\,^1\Delta_u, v=9, 15\leq J\leq 22)+2h\nu \rightarrow (b\,^1\Pi_u, v'=4, J')$$

cannot take place owing to the fact that the selection rule $\Delta J=0,\pm 1,\pm 2$ is not fulfilled for transitions which satisfy energy conditions.

D. Formation of the observed molecular ions N_2^+ and atomic ions N^+

1. *Formation of the molecular ions N_2^+*

The multiphoton ionization of N_2 may be due to various processes. The molecular ion formation

processes from the $v=0$ level of the N_2 ground state $X\,^1\Sigma_g^+$ and from the excited states $a\,^1\Pi_g(v=4)$, $w\,^1\Delta_u$ $(v=9)$, and $b\,^1\Pi_u$ $(v=4)$ are given by the reactions (19) to (32) and schematized in Fig. 6(a):

$$X\,^1\Sigma_g^+ + 14h\nu \rightarrow X\,^2\Sigma_g^+ + e\ , \tag{19}$$

$$X\,^1\Sigma_g^+ + 15h\nu \rightarrow A\,^2\Pi_u + e\ , \tag{20}$$

$$a\,^1\Pi_g + 6h\nu \rightarrow X\,^2\Sigma_g^+ + e\ , \tag{21}$$

$$a\,^1\Pi_g + 7h\nu \rightarrow A\,^2\Pi_u + e\ , \tag{22}$$

$$a\,^1\Pi_g + 9h\nu \rightarrow B\,^2\Sigma_u^+ + e\ , \tag{23}$$

$$a\,^1\Pi_g + 13h\nu \rightarrow C\,^2\Sigma_u^+ + e\ , \tag{24}$$

$$w\,^1\Delta_u + 5h\nu \rightarrow X\,^2\Sigma_g^+ + e\ , \tag{25}$$

$$w\,^1\Delta_u + 6h\nu \rightarrow A\,^2\Pi_u + e\ , \tag{26}$$

$$w\,^1\Delta_u + 8h\nu \rightarrow B\,^2\Sigma_u^+ + e\ , \tag{27}$$

$$w\,^1\Delta_u + 12h\nu \rightarrow C\,^2\Sigma_u^+ + e\ , \tag{28}$$

$$b\,^1\Pi_u + 3h\nu \rightarrow X\,^2\Sigma_g^+ + e\ , \tag{29}$$

$$b\,^1\Pi_u + 4h\nu \rightarrow A\,^2\Pi_u + e\ , \tag{30}$$

$$b\,^1\Pi_u + 6h\nu \rightarrow B\,^2\Sigma_u^+ + e\ , \tag{31}$$

$$b\,^1\Pi_u + 10h\nu \rightarrow C\,^2\Sigma_u^+ + e\ . \tag{32}$$

All these reactions are possible as soon as the energy of K photons plus the potential energy of the initial level is equal to or greater than the potential energy of the final level; the excess of energy in the latter case is carried out by the liberated electron. However, the experiment shows that the value of K is 9 ± 1 for the production of N_2^+, so we must neglect the reactions (19), (20), (24), and (28) which are incompatible with the observed slope. For the remaining reactions we shall keep the most probable ones, i.e., those for which the K value is the smallest, that are reactions (21), (25), and (29). The final level which satisfies the energy conditions is in these cases $X\,^2\Sigma_g^+$ in the vibrational states $v'=0$, 1, 2, or 3. For the transitions $a\,^1\Pi_g \rightarrow X\,^2\Sigma_g^+$ $(v'=0)$, $w\,^1\Delta_u \rightarrow X\,^2\Sigma_g^+$ $(v'=0)$, $b\,^1\Pi_u \rightarrow X\,^2\Sigma_g^+$ $(v'=0)$, the calculated FCF are, respectively, equal to 0.12, 0.05, and 0.28, values which indicate that these transitions are highly probable. The FCF found for transitions from $a\,^1\Pi_g$,$w\,^1\Delta_u$,$b\,^1\Pi_u$ towards $X\,^2\Sigma_g^+$ $(v'=1,2,3)$ are much smaller. Moreover, the selection rules concerning ΔJ, when taking into account the fact that the electron which is ejected has an orbital angular momentum l, becomes $\Delta J=0,\pm1,\ldots,\pm(K+l)$ and we can verify that the coupling is the best for the transition to the $X\,^2\Sigma_g^+$ $(v'=0)$ level. One can conclude that the final level is the level $X\,^2\Sigma_g^+$ $(v'=0)$. The strong three-photon coupling which exists between the $a\,^1\Pi_g$ and $b\,^1\Pi_u$ states leads us to think that the main channel for the depopulation of the $a\,^1\Pi_g$ level is the excitation of $b\,^1\Pi_u$ [reaction (18)] rather than the ionizing reactions (21) to (24). At last, as we can see later, the $b\,^1\Pi_u$ level is found quasicompletely predissociated[16–18] so that the only important way for the production of N_2^+

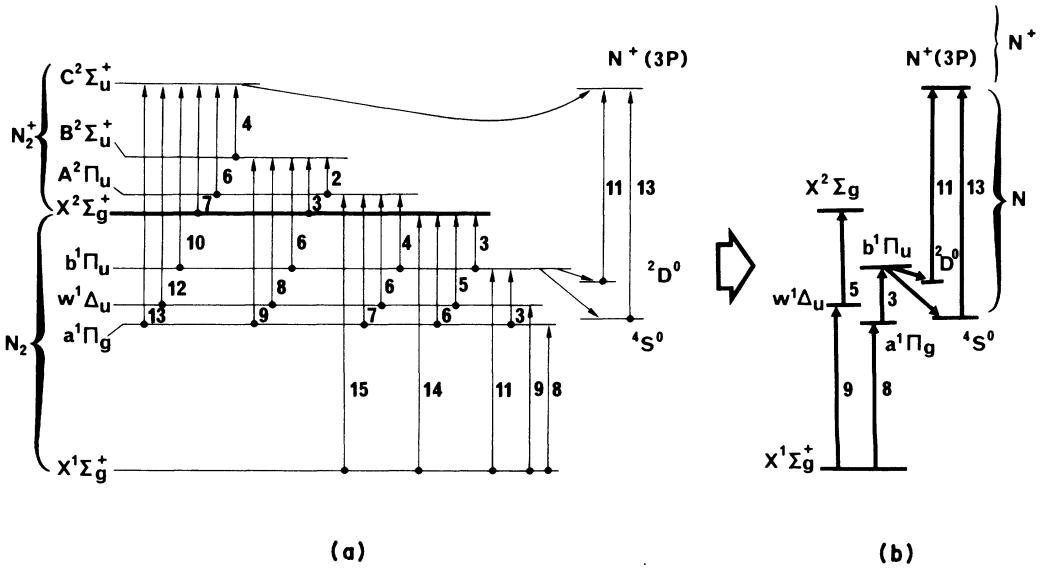

FIG. 6. (a) Diagram of all the possible multiphoton transitions. (b) Main multiphoton transitions for the formation of the ions N_2^+ and N^+.

seems to be the reaction (25), and more precisely

$$w\,^1\Delta_u\ (v=9,15\leq J\leq 22)+5h\nu \rightarrow X\,^2\Sigma_g^+\ (v'=0,10\leq J'\leq 27)+e\ . \tag{33}$$

The $X\,^2\Sigma_g^+$ $(v'=0)$ level can be further excited but in this case there is no change in the final number of ions $N_2{}^+$. The direct ionization of $X\,^2\Sigma_g^+$ needs an interaction with a very great number of photons which is incompatible with the experimental value.

Finally, we can consider that the formation of the molecular ions $N_2{}^+$ is essentially governed by the nine-photon excitation of the $X\,^1\Sigma_g^+$ level towards the $w\,^1\Delta_u$ $(v'=9)$ level [reaction (16)] followed by the five-photon ionization of the $w\,^1\Delta_u$ level towards the $X\,^2\Sigma_g^+$ level [reaction (33)].

The probability of formation of molecular ions $W(N_2{}^+)$ or the effective probability $P(N_2{}^+)\simeq W(N_2{}^+)\tau$, where τ is the laser pulse duration, is usually expressed in the form

$$P(N_2{}^+)=P_{(9)}(X\,^1\Sigma_g^+\rightarrow w\,^1\Delta_u)P_{(5)}(w\,^1\Delta_u\rightarrow X\,^2\Sigma_g^+)\ ,$$

where $P_{(9)}$ is the effective probability of excitation of the resonant level $w\,^1\Delta_u$ from the ground state, involving the absorption of nine quanta, and $P_{(5)}$ is the effective probability of ionization of the level $w\,^1\Delta_u$ by the absorption of five additional quanta.

In the case where none of the two component steps is saturated the power dependence of $W(N_2{}^+)$ or $P(N_2{}^+)$ is equal to the sum of the K values of each component step, i.e., $9+5=14$. But when it happens that $P_{(5)}\simeq W_{(5)}\tau\geq 1$ for some intensity ϕ_0, all the molecules in the $w\,^1\Delta_u$ state in the interaction volume are ionized and $P(N_2^+)$ will be of the order of $P_{(9)}$, i.e., proportional to ϕ_0^9 rather than ϕ_0^{14}. This occurs in our experiment because we find a power dependence of $[N_2{}^+]$ or $W(N_2{}^+)$ equal to nine.

Consequently, the fact that the five-photon process is saturated and that the power dependence of the overall process is equal to the largest K value of the component steps is inferred by the experimental results.

There have been a number of experiments using alkali-metal vapors and atomic and molecular gases which support this view.[19] In particular, the Saclay group has shown, by varying τ, that the power dependence is equal to the sum of the K values of the component steps for $W\tau<1$ and equal to the largest value for $W\tau>1$.

Moreover we can, in this particular case, roughly estimate the value of $P_{(5)}$ by using a simplified expression of ionization probability of an excited level given by Keldysh[20] in a semiclassical formalism. The behavior of multiphoton ionization is related to the parameter γ defined as $\gamma=(\omega/eE)\times(2m\Delta E)^{1/2}$, where ω and E are the angular frequency and peak electric field of the laser radiation, respectively. ΔE is the ionization energy of the $w\,^1\Delta_u$ level, and e and m are the charge and mass of the electron, respectively.

For $\gamma>1$, ionization results only from multiphoton processes with no tunneling effect. We find $\gamma\simeq 3.5$ and $P_{(5)}=W_{(5)}\ \tau>>1$. The transition $w\,^1\Delta_u\rightarrow X\,^2\Sigma_g^+$ is thus saturated.

2. *Formation of the atomic nitrogen ions N^+*

The atomic nitrogen ions N^+ may be produced either by the dissociation of the neutral excited molecules with subsequent ionization of the nitrogen atoms or by the dissociation of the molecular ions $N_2{}^+$. In the second case the only possibility of dissociation of $N_2{}^+$ which appears in our experiment is the predissociation of the level $C\,^2\Sigma_u^+$ $(v=3$ and $v=4)$. These states can be predissociated by the continuum of the $B\,^2\Sigma_u^+$ state through nuclear momentum coupling.[16]

The $C\,^2\Sigma_u^+$ state can be populated by the direct ionization of the excited molecule [reactions (24), (28), and (32)] by a great number of photons—which is a not efficient process, and by the excitation of the $X\,^2\Sigma_g^+$ molecular ion according to the reactions

$$-X\,^2\Sigma_g^+\ (v=3,7\leq J\leq 16)+7h\nu \rightarrow C\,^2\Sigma_u^+\ (v'=4,0\leq J'\leq 16)\ , \tag{34}$$

$$-X\,^2\Sigma_g^+\ (v=2,6\leq J\leq 21)+3h\nu \rightarrow B\,^2\Sigma_u^+\ (v'=3,9\leq J'\leq 22)\ , \tag{35}$$

followed by

$$B\,^2\Sigma_u^+\ (v=3,17\leq J\leq 22)+4h\nu \rightarrow C\,^2\Sigma_u^+\ (v'=3,13\leq J'\leq 22)\ , \tag{36}$$

$$-X\,^2\Sigma_g^+\ (v=3,0\leq J\leq 18)+3h\nu \rightarrow B\,^2\Sigma_u^+\ (v'=4,2\leq J'\leq 18)\ , \tag{37}$$

followed by

$$B\,^2\Sigma_u^+\ (v=4,2\leq J\leq 18)+4h\nu \rightarrow C\,^2\Sigma_u^+\ (v'=4,5\leq J'\leq 18)\ , \tag{38}$$

where the calculated FCF for the reactions (34) to (38) are, respectively, found equal to 0.07, 0.41,

0.03, 0.38, and 0.07.

However, as previously mentioned, the populations of the levels $X\,^2\Sigma_g^+$ ($v=2,3$) represent a very weak part of the total population of N_2^+ mainly concentrated in the $X\,^2\Sigma_g^+$ ($v=0$) state, so that we may neglect the production of ions N^+ by this channel.

The processes leading to N^+ and involving the dissociation of the neutral molecule are firstly the natural predissociation and secondly the laser-induced molecular predissociation[21] (single or multiple, resonant, or nonresonant) which depends on the characteristics of the photon field as frequency, intensity, polarization.

In the case of our experiment, the most important dissociation channel is the natural predissociation of the level $b\,^1\Pi_u$ ($v=4$). Dressler[17] and Carroll and Collins[17] have shown that both in emission and in absorption there is evidence of predissociation in the levels $v=0$, 2, 3, and 4 of the $b\,^1\Pi_u$ state. Recently Zipf and Gorman[18] have shown, in an experiment by electron impact, that all the vibrational levels of $b\,^1\Pi_u$ with the exception of $v=1$, 5, and 6 are found to predissociate with a specific predissociation branching ratio >0.99.

From simple energy consideration the atomic products are $^4S^o+^2D^o$ and $^4S^o+^4S^o$. The mechanism responsible for the predissociation of $b\,^1\Pi_u$ is not completely explained but it is sure that it involves an intersystem radiationless transition from the singlet $b\,^1\Pi_u$ to the triplet states $^3\Pi_u$,$C'\,^3\Pi_u$, $A\,^3\Sigma_u^+$, $^3\Delta_u$. This predissociation process forbidden by the Kronig's selection rules is a major source of the nitrogen atoms produced by multiphoton dissociation of N_2. The resulting atoms $^4S^o$ and $^2D^o$ would then be, respectively, ionized through the simultaneous absorption of 13 photons or 11 photons.

The second possible decomposition channel is the photon-induced predissociation introduced by Lau.[21] The molecules in the discrete states can make electric dipole transitions to the predissociative continuum by stimulated absorption or emission of one or two photons. The single-photon stimulated decomposition seems possible on the $a\,^1\Pi_g$ and $b\,^1\Pi_u$ states via the $A\,^3\Sigma_u^+$ and $G\,^3\Delta_g$ states, respectively. In the two-photon electric dipole transition or photocatalytic effect PCE (the stimulated transition is without actual absorption or emission of laser photons), the transitions take place from the bound initial state to the continuum of dissociation via a near-resonant level. This effect is possible mainly at the lowest order on the $w\,^1\Delta_u$ state via the $a\,^1\Pi_g$ resonant intermediate state to the $A\,^3\Sigma_u^+$ continuum state. We have no theoretical result to verify that for the laser intensity of $\simeq 2\times 10^{12}$ W/cm^2 and pulse duration about 3×10^{-8} sec used in the experiment, the molecules N_2 could be photocatalyzed during the laser pulse.

Finally we can consider that the formation of the atomic ions N^+ is essentially governed by the eight-photon excitation of the $X\,^1\Sigma_g^+$ level towards the $a\,^1\Pi_g$ ($v=4$) level [reaction (14)] followed by the three-photon excitation of the $a\,^1\Pi_g$ level towards the $b\,^1\Pi_u$ ($v=4$) level [reaction (18)] which is predissociated in atoms. These atoms are subsequently ionized by absorption of 11 or 13 photons.

Just as it has been done for the production of molecular N_2^+ ions, the effective probability of production of atomic N^+ ions is written

$$P(N^+)=P_{(8)}(X\,^1\Sigma_g^+\rightarrow a\,^1\Pi_g)P_{(3)}(a\,^1\Pi_g\rightarrow b\,^1\Pi_u)\times P_{(D)}(b\,^1\Pi_u\rightarrow N)P_{(11\text{ or }13)}(N\rightarrow N^+)\,,$$

where $P_{(8)}$ is the rate of the multiphoton transition between the ground and the $a\,^1\Pi_g$ levels, $P_{(3)}$ the rate of transition between the $a\,^1\Pi_g$ and $b\,^1\Pi_u$ levels, P_D the dissociation rate of the $b\,^1\Pi_u$ state, and $P_{(11\text{ or }13)}$ the rate of ionization for the nitrogen atoms in the $^2D^o$ or $^4S^o$ states, respectively.

The factor $P_{(D)}$ ($b\,^1\Pi_u\rightarrow N$) has been measured[18] and found $\simeq 1$. The rates of multiphoton excitation of the molecule $P_{(8)}$ and $P_{(3)}$ are not known and their values are to be derived from the determination of the transition matrix elements. This theoretical understanding is very complicated and is out of the framework of this experimental paper.

Nevertheless it seems reasonable to assume that $P_{(8)}$ and $P_{(3)}$ are ≥ 1 because the power dependence of the overall process $P(N^+)$, i.e., $[N^+]=P(N^+)N_0$ (where N_0 is the number of neutral molecules in the interaction volume before interaction) is found equal to 12 ± 1 and not to a greater value as it would be expected if the intermediate components were not saturated. The assumption that lower-order component steps are saturated is consequently, in this case, deduced from the experiment.

It is worthy of note that in a rough experiment where the ionized particles are collected without discrimination between N^+ and N_2^+ and taking into account the influence of the impurities,[8] the nonlinear order of interaction was found equal to 13 ± 2. This is justified by the fact that the number of atomic ions is about four times greater than the number of molecular ions and the measured slope K concerns essentially the atomic ions.

IV. CONCLUSION

To summarize,[22] our findings are as follows: The MPI of nitrogen by a laser radiation at wavelength of 1.06 μm leads to the production of molecular nitrogen ions N_2^+ and atomic nitrogen ions N^+. The produced ion's quantities are proportional to ϕ_0^K, where ϕ_0 is the maximum laser flux and K is the nonlinear order interaction which is found equal to 9 ± 1 for N_2^+ and 12 ± 1 for N^+. The MPI probabilities determined for a laser flux ϕ_0 equal to 2.44×10^{12} W/cm^2 are, respectively, $W(N_2^+)\simeq3\times10^{6\pm0.7}$ sec^{-1} and $W(N^+)\simeq2\times10^{7\pm0.7}$ sec^{-1}. The MPI cross sections deduced are, respectively, equal to $\sigma_9^{(M)}\simeq3\times10^{-111}$ W^{-9} cm^{18} sec^{-1} for N_2^+ and $\sigma_{12}^{(A)}\simeq9\times10^{-151}$ W^{-12} cm^{24} sec^{-1}. The experimental results can be explained by the following multiphoton absorption processes which are summarized in Fig.6(b).

Production of N_2^+:

$$X\,^1\Sigma_g^+\ (v=0)+9h\nu\rightarrow w\,^1\Delta_u\ (v'=9)$$

followed by

$$w\,^1\Delta_u\ (v=9)+5h\nu\rightarrow X\,^2\Sigma_g^+\ (v'=0)+e\ .$$

Production of N^+:

$$X\,^1\Sigma_g^+\ (v=0)+8h\nu\rightarrow a\,^1\Pi_g\ (v'=4)$$

followed by

$$a\,^1\Pi_g\ (v=4)+3h\nu\rightarrow b\,^1\Pi_u\ (v'=4)\ ,$$

which dissociates in

$$b\,^1\Pi_u\ (v=4)\rightarrow\begin{cases}{}^4S^o+{}^4S^o\ ,\\ {}^4S^o+{}^2D^o\ ,\end{cases}$$

and finally

$${}^2D^o+11h\nu\rightarrow N^+ +e\ ,$$

$${}^4S^o+13h\nu\rightarrow N^+ +e\ .$$

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