Experimental determination of the fraction of the captured particles and of the excitation level in multiphonon excitation of molecules by infrared laser radiation

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Simple experimental methods are proposed for the determination of the principal parameters, namely the fraction of the excited particles and the excitation level, of multiphoton absorption in an IR laser field. The dependences of these quantities on the frequency and energy density of the laser radiation are obtained for the first time ever.

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1. Multiphoton absorption of polyatomic molecules in a strong pulsed IR laser field is the basis for the phenomenon of multiphoton dissociation.[1] Despite the numerous experimental and theoretical studies devoted to the accumulation of molecular energy in an IR laser field, this process is presently understood only qualitatively. The quantity measured in experiment up to now was the average number of photons per molecule of the absorbing gas $\langle n \rangle = E_{abs}/\hbar\omega N_0$ (E_{abs} is the absorbed energy, N_0 is the total number of molecules in the irradiated volume, $\hbar\omega$ is the energy of the laser-radiation quantum). The absorbed energy $\langle n \rangle$ characterizes the process of multiphoton absorption only very approximately, since $\langle n \rangle$ is the fraction q of the molecules captured by the laser radiation, multiplied by the average energy acquired by an individual molecule, i.e., by the excitation level l. Since both factors are functions of E_{las}, we cannot use $\langle n \rangle$ for a theoretical interpretation of the process. For a comparison of the experiment with the calculations, which always deal with an isolated molecule in the IR laser field, it is necessary to measure directly the quantities q and l, and also their dependence on the parameters of the laser radiation, and not obtain numerical values on the basis of the dissociation model. Knowledge of these quantities is the basis for the understanding of the processess of excitation of low- and high-lying vibrational-rotationals states.

In this paper we propose and realize simple experimental approaches which make it possible to measure directly these quantities. The approaches are based on the dissociation of polyatomic molecules in a two-frequency IR laser field, which we have proposed earlier.[2] For OsO_4 molecule we measured experimentally the following: the fraction q of the molecules excited by the laser radiation, the excitation level l, as well as their dependences on the frequency and on the energy density of the laser radiation.

2. The measurement of the energy absorbed by the OsO_4 molecule was carried out with both single-particle and two-particle excitation with CO_2-laser radiation. The pulses from both lasers had a standard shape: a peak of 90 nsec at half-height and a "tail" of $\sim 1.5\,\mu$sec. In the case of two-frequency excitation, the radiation beams were

guided into the cell opposite to each other. To eliminate the mutual influence of the lasers, the radiation was directed into the cell through diffraction gratings. The dissociation yield was monitored against the visible luminescence of the radicals produced in the course of the dissociation, as well as directly, while the IR was monitored spectrometrically. A more detailed description of the experimental setup is given in Ref. 3.

3. *Determination of q and l by saturating the dissociation yield.* The fraction q of the molecules excited by the laser radiation can be determined by excitation with a resonant (ν_1) IR laser field followed by dissociation with a nonresonant (ν_2) IR laser field. If all the excited molecules are dissociated in this case (saturation of the dissociation yield), then the fraction q of the molecules excited by the resonant laser field ν_1 gives directly the dissociation yield. Figure 1 shows plots of the dependence of the
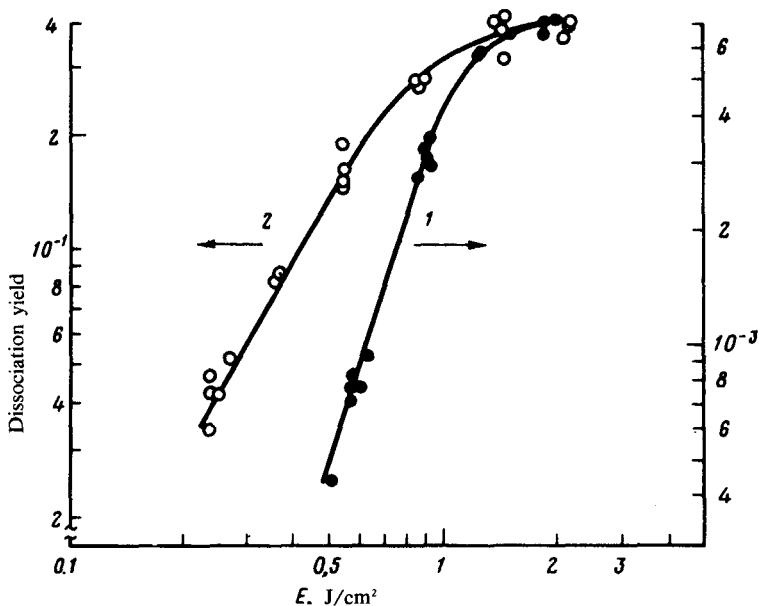

FIG. 1. Dependence of the dissociation yield on the energy density of the laser radiation: curve 1—single-particle excitation $\nu_1 = 927.0$ cm^{-1}, curve 2—two-frequency excitation $\nu_1 = 947.7$ cm^{-1}, $\nu_2 = 927.0$ cm^{-1}. The energy density of the exciting radiation was fixed at $E_1 = 1.2$ J/cm^2. The OsO$_4$ pressure was 0.03 Torr.

dissociation yield of the molecules OsO$_4$ in the case of single-frequency (curve 1) and two-frequency (curve 2) excitation with CO$_2$-laser radiation, obtained under yield-saturation conditions. The dissociation yield saturation in the single-frequency case is attained only by excitation of the far long-wave edge of the P branch of the IR absorption specturm of OsO$_4$ [the $P(38)$ line of the CO$_2$ laser]. A general approach to obtaining saturation of the dissociation yield with excitation on any section of the IR absorption spectrum is dissociation in a two-frequency IR laser field: the excitation is carried out by resonant radiation at the frequency ν_1, and the dissociation by nonresonant

radiation ν_2, tuned away from the linear IR absorption spectrum into the long-wave region.

Figure 2 (curve 1) shows the dependence of the fraction of the excited molecules q
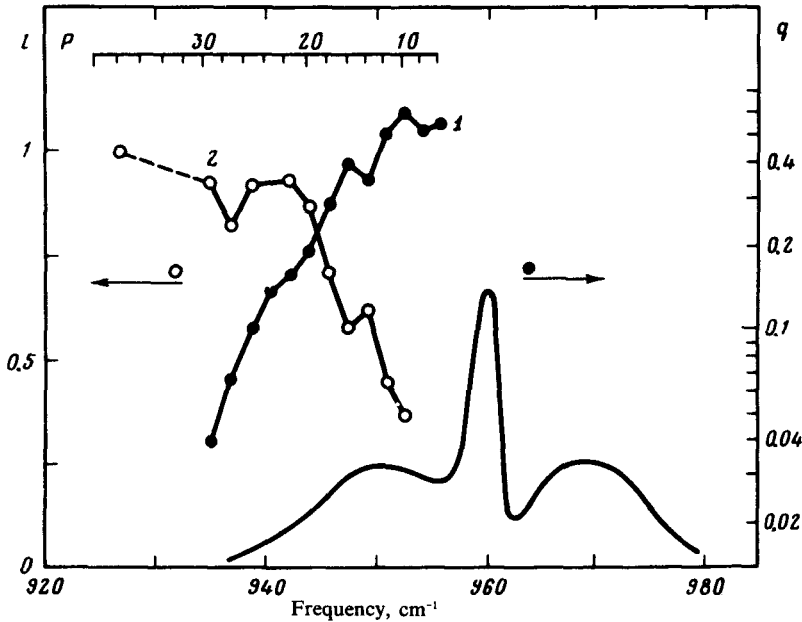

FIG. 2. Dependence of the fraction q of the excited particles and of the excitation level l (in fractions of the dissociation energy D) on the frequency of the exciting radiation. $\nu_1 = \nu_2 = 927.0$ cm^{-1}, $E_1 = 1.2$ J/cm^2, $E_2 = 1.8$ J/cm^2. $P = 0.03$ Torr. The IR absorption line spectrum of OsO_4 is shown for comparison.

on the frequency of the exciting laser radiation. The absolute reconciliation was carried out by measuring the absorbed energy $\langle n \rangle$ upon excitation by the P (38) line of the CO_2 laser, for which under yield-saturation conditions we have $\langle n \rangle = qD$, where D is the dissociation energy ($D = 27$ IR photons). Curve 1 of Fig. 3 shows the dependence of q on the energy density of the laser radiation per measurement of the average number $\langle n \rangle$ of photons per OsO_4 molecule as a function of the frequency and of the energy density of the laser excitation makes it possible to determine the functions $l(\omega)$ and $l(E_{las})$ from the given relations $q(\omega)$ (Fig. 2, curve 1) and $q(E_{las})$ (Fig. 3, curve 1). These relations are shown in Fig. 2 and in Fig. 3 (curve 2).

4. *Determination of q, l, and D by measuring multiphoton absorption in two-frequency dissociation under conditions of yield saturation.* Measurement of multiphoton absorption of resonant exciting and nonresonant dissociating laser radiation when the dissociation yield is saturated makes it possible to determine directly the values of q and l, as well as the dissociation energy D. In fact, the average number of photons absorbed from the exciting laser field at the frequency ν_1 is
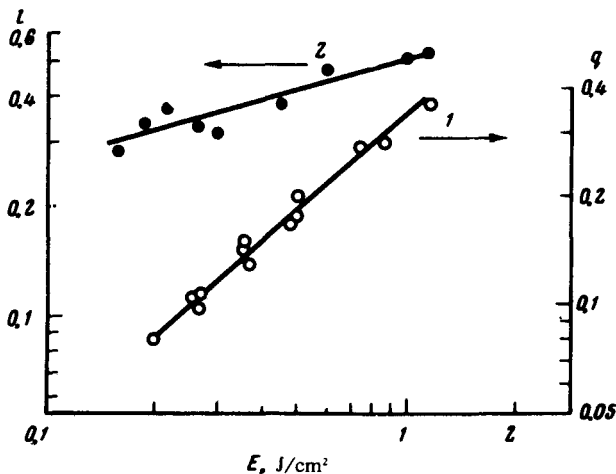
FIG. 3. Dependence of the fraction q of the excited particles and of the excitation level l (in fractions of the dissociation energy D) on the energy density of the exciting radiation. $\nu_1 = 947.7$ cm^{-1}, $\nu_2 = 927.0$ cm^{-1}, $E_2 = 2$ J/cm^2.

$$< n_1 > = ql, \tag{1}$$

and the number absorbed from the dissociating field at the frequency ν_2 at saturated dissociated dissociation yield:

$$< n_2 > = q(D - l). \tag{2}$$

Following distribution of the vibrational excitation, as the result of the $V–V$ exchange over all the molecules, we have for $\langle n_2^* \rangle$ after a lapse of time $\Delta\tau_{V-V}$:

$$< n_2^* > = S(D - ql) = S(D - < n_1 >), \tag{3}$$

where S is the saturation parameter ($S = 1$ upon saturation of the dissociation yield). The equalities (1)–(3) make it possible to determine the sought values of q, l, and D from the measured values of $\langle n_1 \rangle$, $\langle n_2 \rangle$, $\langle n_2^* \rangle$. Such a measurement was performed for the OsO$_4$ molecule at a pressure 0.2 Torr. The frequencies of the exciting and dissociating radiations were 947.7 and 927.0 cm^{-1}, respectively. The number of photons absorbed per molecule from the first field was $\langle n_1 \rangle = 5.3$ ($\tau_p = 90$ nsec plus a 1.5- μsec "tail;" $E_1 = 1.0$ J/cm^2, $E_2 = 2.0$ J/cm^2) or $\langle n_1 \rangle = 0.8$ ($\tau_p = 90$ nsec, $E_1 = 0.3$ J/cm^2, $E_2 = 2.0$ J/cm^2). The corresponding $\langle n_2 \rangle = 14$, and $\langle n_2^* \rangle = 18$ after establishment of equilibrium ($\Delta\tau_{VV} \approx 10$ sec). These values yield $q \approx 0.7$, $l \approx 7$, and $D = 23 \pm 5$. Similarly, for excitation by a short pulse we have $q \approx 0.2$ and $l \approx 5$.

Our investigation has shown that both procedures make it possible to determine the real parameters of multiphoton absorption, namely the fraction q of the excited molecules and the excitation level l, as well as their dependences on the laser-radiation parameters: $q(\omega, E_{1as})$ and $l(\omega, E_{1as})$.

Knowledge of $q(E_{1as})$ has made possible a comparison of the observed dissociation yield with a calculation based on two models: a simple thermal model[4] and a kinetic model.[5] In the calculation of the kinetics of the excitation of the OsO_4 molecule by laser radiation, the cross section of the successive transition $\sigma(i)$ (i is the number of absorbed photons) was chosen such that the $q(E_{1as})$ relation agreed with the calculated one: $\sigma(i) = \exp(-0.0885i - 41.36)$ cm^2. Calculation of the excitation kinetics with the cross sections chosen in this manner gives a dissociation yield which agrees well with those observed in experiment. The thermal model gives a more gently sloping decrease of the dissociation yield with decreasing energy of the laser radiation, thus indicating that the distribution of the molecules in the real case terminates more steeply than a Boltzmann distribution on the side of the high vibrational levels. These results confirm an analogous conclusion[5] for the SF_6 molecule.

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