Ion production by IR laser irradiation of polyatomic molecules and electric isotope separation

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(Submitted June 19, 1975)
Pis'ma Zh. Eksp. Teor. Fiz. **22**, No. 2, 100–102 (July 20, 1975)

The presence of a quasicontinuous sequence of levels of polyatomic molecules with high degree of excitation explains the effect of "instantaneous" dissociation and leads to the conclusion that the "instantaneous" ion production can occur when an intense IR laser radiation acts on molecules. This effect can be used for isotope separation.

PACS numbers: 32.20.M, 42.60.Q

In the case of resonant excitation of vibrational levels of molecules by IR laser radiation, the main mechanism of the redistribution of the resonantly absorbed energy is usually assumed to be the collisions.[1,2] Yet an "instantaneous" (collisionless) molecule dissociation was recently[3,4] observed experimentally in the field of intense IR laser radiation, within times shorter than the time of vibrational V-V exchange. It is obvious that an essential role is played here by the radiative mechanism of excitation of higher vibrational levels.

We deduce in this communication, on the basis of an analysis of the radiative mechanism of the action of resonant radiation on polyatomic molecules, the feasibility of an effect of "instantaneous" ionization of moleocules by radiation having quanta much lower than the dissociation energy (and, by the same token, ionization energy) of the molecules, and also consider the possibility of electrically separating isotopes of laser-irradiated molecules.

In polyatomic molecules such as BCl_3, SF_6, etc., the total number of vibrational levels, including combination levels, corresponding to excitation of S vibrational quanta in l vibrational modes, is given by the binomial coefficient C^s_{s+l+1}, and is high enough at a high degree of excitation. Allowance for the rotational structure causes the average distance between levels, at the excitation level corresponding to (3 to 4)$h\nu$, to become commensurate with the homogeneous width of the rotational level, and the levels coalesce into a single quasicontinuous background. It then becomes possible to excite these levels in succession, in steps equal to the energy $h\nu$ of the exciting laser quantum which is resonant to the transition from the ground to the first-excited vibrational state. By virtue of the anharmonicity, the molecules following the second or third level drop out of the resonances, but their passage is possible in the case of sufficiently intense laser irradiation that leads to level "broadening" by the field.

Thus, pure radiative excitation of the higher vibrational levels of polyatomic molecules is possible, up to dissociation, and upon excitation of several of the low-lying levels there is realized the case of large detunings, but of allowed transitions, whereas population of the higher levels leads to forbidden resonant transitions.

Located above the dissociation boundary is the region of the electron-vibrational-rotational levels, which is also characterized by a high density of states. The number of electronic terms for polyatomic molecules of the type BCl_3, SF_6, or SiF_4 exceeds 10^2. These terms are divided into binding and spreading. For the binding terms, the most probable structure is one in which a higher potential well enters in the interior of a lower one, as in a number of diatomic molecules.[5] This results in a quasicontinuous sequence of vibrational-rotational levels up to the ionization limit. Then, if only the binding terms are taken into account, radiative excitation becomes possible in resonant transitions in the quasicontinuous sequence of levels, in analogy with the situation in the sequence of the levels of the electronic ground state. Thus the radiation corresponding to the vibrational quanta of the molecule populates the vibrational levels of the excited electronic states of the molecules. "Instantaneous" ionization is realized as a result.

The landing of the molecule on different terms (lifetime $\sim 10^{-15}$ sec) means its decay and emergence from the radiative-excitation channel. It must be borne in mind, however, that owing to the large width of the spreading term (~1 eV), transitions to these terms have low probability. Nevertheless this channel must be taken into account, as well as the nonadiabatic processes that occur on the binding terms. It appears that the unusual products of the "instantaneous" dissociation, which were observed experimentally,[6] can be attributed to the strong overexcitation of the molecule in comparison with its excitation within the limits of the electronic ground state. In addition, the fragments obtained upon dissociation of strongly overexcited molecules are easily ionized, as a result of which both channels lead to the effect of "instantaneous" collisionless ion production.

A preliminary experiment has shown that ions and electrons are produced in BCl_3 gas at pressures from 0.01 to 0.1 Torr following irradiation by pulses of focused CO_2-laser radiation of 200 nsec duration and 10^7–10^8 W power.

Since the considered process begins with resonant excitation of the first vibrational level, the selectivity of the excitation is preserved up to the ionization. This can be used to separate the isotopes by an electric field. We must bear in mind here the need for excluding colli-

sions, say by using molecular beams. In addition, the intensity of the laser radiation must be sufficient to "broaden" the level of the molecules of one isotopic composition, but insufficient for effective excitation of molecules of another composition.

A theoretical analysis of "instantaneous" ionization and dissociation has led to the conclusion that there exist both a laser-intensity threshold and a threshold for the integral of the pulse envelope. Once the thresholds are exceeded, the populations are distributed, on the average, approximately uniformly over all the energy levels that are multiples of $h\nu$. In the possible case of a break in the quasicontinuous sequence of the levels, the passage through the corresponding energy level can lead to the existence of a threshold intensity, which is characteristic of multiphoton processes.

It is useful to note that radiative excitation of molecules by IR laser radiation up to ionization may be an effective method of obtaining electron-excited molecules for the stimulation of chemical reactions, particularly for large molecules and biological objects.

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