exploited the use of different constant rotation speeds by extrapolating current data to infinite rotation speed $(1/\omega \rightarrow 0)$, thus eliminating the difference between surface and bulk concentrations.

These rotating solid electrode techniques are still subject to interferences from nonfaradaic and time-varying surface-process currents. Therefore, despite their inherent advantages of high sensitivity and different potential range, they have always suffered when compared to the atomically smooth, constantly renewing dropping mercury electrodes. Hydrodynamic programming, particularly in the SHM mode at the RDE, has made great strides in eliminating many solid electrode disadvantages. The unique prospects of controlled surface concentrations via ω–f(i) program-

ming have added to the controlled potential and current techniques for electrochemical studies. Also $\omega^{-1/2}$ control now provides a variable comparable to time.[29]

It is apparent from the list of RRDE applications that the virtually instantaneous analysis of the diffusion layer provided by the ring adds immensely to the range of chemical and mechanistic problems that can be studied. Also the complementary relationship of the RRDE and hydrodynamic voltammetric methodologies suggests that even more subtle problems can be attacked by applying the methods in concert.

Selective Dissociation of Polyatomic Molecules by Intense Infrared Laser Fields

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Received July 22, 1976

In this Account we discuss the specific features of the isotopically selective dissociation of polyatomic molecules (BCl_3,[1] SF_6,[2] OsO_4,[3] etc.) by intense CO_2 laser pulses. The effect was discovered in 1974 in our laboratory. Though for some people our discovery was perhaps unexpected, for us it was, in fact, a logical and related result of our work on the isotopically selective dissociation of molecules by laser radiation. Accordingly, a short review of the development of our work is appropriate here.

In 1970 we began systematic studies of isotopically selective molecular dissociation based on selective excitation of molecular vibrational levels and subsequent dissociation of selectively excited molecules by UV radiation (two-step IR–UV dissociation). The first results of this work were reported in 1971 at the CLEA conference,[4] and after a year our laboratory realized what was perhaps the first successful isotope separation (^{14}N and ^{15}N) by the method of two-step selective dissociation of molecules (NH_3).[5] At approximately the same time we realized that in some cases isotopically selective dissociation was possible in a one-step process owing to the effect of predissociation.[6] The first successful experiment on isotope separation by this technique was also carried out in 1972, by Yeung and Moore.[7] Thus, in addition to the well-known photo-

chemical approach to isotope separation, a new photodissociation method was developed (see reviews[8,9]). This method has basic advantages over the photochemical one as far as high selectivity is concerned, because it employs chemical binding of dissociation products and does not necessitate special selection of a fast reaction of selectively excited atoms or molecules.[10]

In 1971 we began studying the visible luminescence of molecular gases pumped by focused CO_2 laser pulses. This phenomen had been observed by Isenor and Richardson[11] not long before. We made a detailed study of the kinetics and spectra of luminescence of NH_3 and C_2F_3Cl molecules pumped by transversely excited atmospheric pressure (TEA) CO_2 laser pulses[12,13] (similar experiments are described in ref 14). In this

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work, the nonthermal nature of molecular dissociation and the small contribution of collisions to dissociation and luminescence were demonstrated. N_2F_4 molecules dissociated when irradiated by CO_2 laser pulses under conditions where the collisional effects could not be neglected.[15] Suspecting that the main contribution to molecular dissociation in our experiments was made by an intense IR field rather than by a thermal effect, we attempted to prove this in 1972 with experiments on the dissociation of $^{15}NH_3$ molecules mixed with $^{14}NH_3$, using focused pulses of a TEA–CO_2 laser. These experiments gave negative results. After that, we decided to investigate in more detail the process of dissociation on a more suitable molecule, BCl_3. In special experiments on BCl_3 at extremely low pressures, both collisionless dissociation of the molecules in an intense IR field and a collisional contribution to the dissociation of excited molecules were observed.[16] Similar results were obtained by Canadian researchers in experiments on SiF_4 molecules.[14] The next logical step in our experiments was the observation of high isotopic selectivity in the dissociation of BCl_3 molecules, by examining the isotope effect in the chemiluminescence of the BO radical formed in the reaction of dissociated fragments with O_2.[1] This was of vital importance from two standpoints: first, it became clear that the process of dissociation of an isolated molecule by an intense IR field is a result of the interaction of the IR field with molecular vibrations only, without any collisional contribution; second, we obtained another very efficient and simple method of isotope separation, within the photodissociation approach to laser isotope separation, which we are developing now.

Collisionless and Collisional Dissociation of BCl_3

Studies of the luminescence kinetics of electronically excited radicals formed in the dissociation process carried out at very low pressures of BCl_3,[16] such that the time between two successive collisions was much longer than the laser pulse duration, have enabled us to draw the following qualitative picture of the kinetics of molecular dissociation in an intense IR field.

Having absorbed a large amount of energy (about several electron volts) from the IR field in the collision-free regime, some of the molecules dissociate almost instantly, without any collisions. The remaining molecules, also having accumulated a considerable energy from the field, remain at high vibrational levels and dissociate during collisions.

The effect of collisionless energy storage through step-by-step absorption of a large number of infrared quanta is not trivial from the physical standpoint, if we consider that because of anharmonicity a molecule will be out of absorption resonance if it absorbs even one photon from the IR field. Yet, in order to dissociate, a molecule usually requires an energy of the order of several electron volts; that is, it must absorb several dozen to a hundred IR photons.

The strong dependence of the BCl_3 dissociation on the exciting IR field frequency observed[16] was a very

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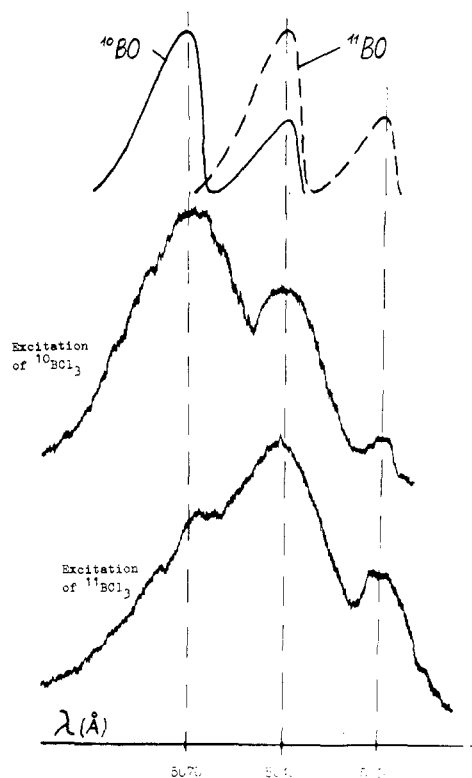
Figure 1. Chemiluminescence spectrum of BO formed after the dissociation of BCl_3 molecules by an intense IR field: (a) schematic position of lines of BO radicals (α band); (b) laser radiation excites $^{10}BCl_3$ molecules; (c) laser radiation excited $^{11}BCl_3$ molecules; (BCl_3 pressure 4 Torr, oxygen pressure 5 Torr, nitrogen pressure 15 Torr).

important fact. When the laser frequency was tuned away from the ν_3 absorption band, the BCl_3 dissociation disappeared.

If molecular dissociation is usually a result of vibrational energy storage, the molecules of one isotopic species can dissociate during selective excitation, at least in the stage of collisionless dissociation when there is no V–V transfer. Then, since the kinetic data show that dissociation during the collisional stage is induced by a small number of collisions, it is also expected to be isotopically selective, provided that molecules of the same isotopic composition are selectively excited initially.

The best way of testing the correctness of such an approach was to observe chemical reactions between the dissociation products of BCl_3 molecules and oxygen added to the reaction vessel in which BCl_3 molecules were dissociated by an intense IR field.[1] The intense chemiluminescence of the BO radicals produced by this reaction made it possible to study the isotopic selectivity of dissociation during the formation of chemically unstable radicals.

Figure 1 shows the luminescence spectra of the radicals formed (a) when the frequency of an intense CO_2 laser was tuned to the $^{10}BCl_3$ absorption band and (b) when $^{11}BCl_3$ molecules are excited by the laser. On the top a normalized spectrum of the BO radical (α band) is shown. It can be seen from Figure 1 that the isotope composition of ^iBO radicals corresponds to the composition of excited $^iBCl_3$ molecules.

From these spectral data on BO chemiluminescence, one can evaluate the selectivity of BCl_3 dissociation (or the enrichment coefficient of reaction products) for a

specified isotope under given experimental conditions. The dissociation selectivity is defined as

$$S = \frac{[^{10}BO][^{11}BCl_3]}{[^{11}BO][^{10}BCl_3]} \qquad (1)$$

We find from the experimental data that $S \simeq 10$, in the case when the $^{10}BCl_3$ molecules were excited by the R(24) line of a CO_2 laser. The dissociation selectivity was found to be the same both during the collisionless and collisional stages.[17]

The experiment shows that even at rather high pressures the dissociation selectivity is high, and molecular dissociation occurs because of energy storage in the vibrational degree of freedom and is not a result of the possible nonresonant interaction of a molecule with free electrons which can acquire energy from the laser field. In the latter case the dissociation would not be isotopically selective.

Note that when conducting experiments on BCl_3 one should carefully choose a chemical reaction for scavenging radicals formed in the dissociation process. Because of this, in experiments on boron enrichment it is difficult to take quantitative account of the role of selectivity loss in subsequent chemical reactions, and when there is no scavenger added the reverse reaction occurs. Our experiments on boron enrichment in macroscopic amounts by this technique show that the enrichment coefficient in the reaction products varies from 2 to 20 depending on the added scavenger.[18]

After the experiments on isotopically selective dissociation of BCl_3 molecules carried out in 1974 it was obvious that the effect was general in nature and could take place in many polyatomic molecules.

At present we have obtained much information on isotope separation by the dissociation caused by multiple IR photon absorption method in several molecules (BCl_3,[1,17] SF_6,[2] OsO_4,[3] CCl_4,[19] SiF_4,[20] CF_2Cl_2,[20] etc.). The dissociation process of SF_6 was studied most carefully. These studies enabled us to understand the nature and basic characteristics of both selective dissociation and isotope separation by this process.

Isotopically Selective Dissociation of SF_6 and Isotope Separation

In the first experiments[2] on the selective dissociation of SF_6 of natural isotopic abundance, the enrichment coefficient in residual undissociated SF_6 with the isotope ^{34}S (in the form of $^{34}SF_6$) in relation to $^{32}SF_6$ was over 10^3 and in a number of subsequent experiments[21] it exceeded 10^4. The enrichment factor measured in residual products (nondissociated absorber) is associated with the kinetics of enrichment (dissociation).[22] This can be understood if we take into account the fact that molecules of different isotopic composition dissociate with different relative rates. The enrichment
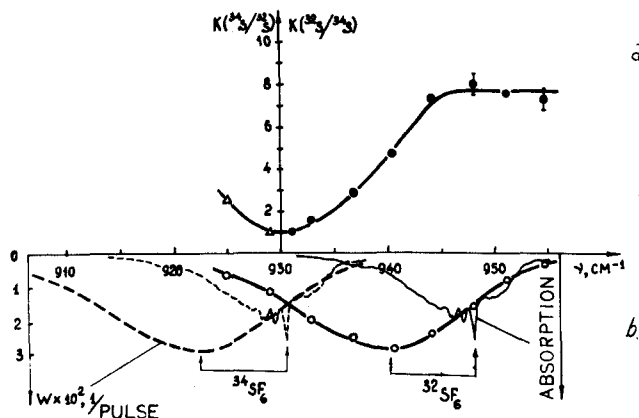

Figure 2. (a) Dependence on dissociating field frequency of the isotopic selectivity S or the enrichment coefficient in the reaction product (SOF_2) formed after dissociation of SF_6 molecules. (b) Dependence of dissociation rate W of $^{32}SF_6$ molecules on laser radiation frequency. Linear IR absorption spectrum of SF_6 is shown by solid lines. Expected analogous dependence for $^{34}SF_6$ molecule and its linear IR spectrum are shown by dashed lines.

coefficient in the residual undissociated gas may be made as high as one wants by changing the extent of dissociation of the initial reactant. The enrichment coefficient in the residual gas is given by the expression[22]

$$K_{res}(b/a) = \left(\frac{N_b}{N_a}\right) \Big/ \left(\frac{N_{b0}}{N_{d0}}\right) = \exp\left(\frac{S-1}{S} W_i t\right) \qquad (2)$$

where $S = W_a/W_b$ is the ratio of dissociation rates of two isotopically different molecules (a and b), that is, the dissociation selectivity; t is the time of irradiation or the number of irradiation pulses; and W_i is the dissociation rate describing the decrease of the gas component i, defined as

$$N_i = N_{i0} \exp(-W_i t) \qquad (3)$$

where N_i and N_{i0} denote current and initial molecular concentration of i molecules in the reactor. This suggests that the main parameter of the process is the dissociation selectivity. As noted above, in the case of BCl_3 under given experimental conditions the dissociation selectivity S was equal to 10.

For direct evaluation of S it is enough to measure the isotopic enrichment in the resultant dissociation products M_i:

$$K_{prod}(a/b) = \left(\frac{M_a}{M_b}\right) \Big/ \left(\frac{N_{d0}}{N_{b0}}\right) = \frac{1 - \exp(-W_a t)}{1 - \exp\left(-\frac{1}{S} W_a t\right)} \qquad (4)$$

The value K_{prod} exactly coincides with dissociation selectivity S if the amount of dissociated gas is small ($W_a t \ll 1$):

$$K_{prod} = S \qquad (5)$$

There is some evidence[23] that in an intense IR field the SF_6 molecule dissociates mainly to SF_4 and F_2, although the dissociation products are strongly dependent on laser intensity.[24] Mass spectrometric

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(24) K. H. Kompa, talk presented at Tunable Lasers and Applications International Conference, Loen, Norway, June 7–11, 1976.

analysis of SF_4 in the presence of SF_6 is rather difficult because of overlapping of the mass peaks. Therefore, it is easier to do mass analysis on SOF_2, the product of hydrolysis of SF_4. The hydrolysis of SF_4 occurs rapidly.

Of most interest are the dependence of the dissociation selectivity S on the IR laser frequency at which dissociation occurs and its correlation with the low-power IR absorption band shape of SF_6. Such a frequency dependence of the enrichment coefficient of SOF_2 formed as a result of dissociation[25] is given in Figure 2b. This figure shows the dissociation rate dependence of $^{32}SF_6$ on laser frequency. It is obvious that when the dissociation rates W_i for both the isotopic molecules become equal, no enrichment is expected. The dashed line in this figure is for the assumed frequency dependence of the $^{34}SF_6$ dissociation rate. The comparison with Figure 2a shows that near the intersection point of the dissociation rate curves the enrichment coefficient equals unity, which means that there is no enrichment here. A shift up or down from this frequency gives enrichment of one or another isotope in the reaction product (SOF_2). The highest dissociation selectivity measured at 0.05 Torr is $S = 14$. (Actually S is probably much higher, for the value obtained depends on the natural $^{34}S/^{18}O$ ratio, since the mass analysis of SOF_2 was carried out with low mass resolution.)

Our previous investigations showed that molecules store energy in a pulsed field (in the purely collisionless regime) in proportion to $I^{0.8}$, where I is the resonance field intensity, and on reaching the dissociation limit this dependence is changed to $I^{1/2}$. Such a relation between the number of absorbed quanta $\langle n \rangle$ per molecule

$$\langle n \rangle = \frac{E_{abs}}{\hbar \omega N_0} \tag{6}$$

and the radiation intensity is given in Figure 3, where E_{abs} is the energy absorbed in the irradiated volume, and N_0 is the total number of molecules in the volume. It should be noted that the fraction of molecules which have really interacted with the field absorb, obviously, many more photons than indicated by eq 6. The number of molecules interacting with the field is not exactly known, however, and we have therefore to use the value $\langle n \rangle$ introduced above (eq 6). Figure 3b represents the dependence of the dissociation rate W_a on incident intensity. In contrast to the dissociation, the vibrational excitation to the high-lying states has no intensity threshold. It is clear, therefore, that the dissociation threshold is associated not with the elimination of anharmonicity in the first vibrational levels but rather with the nonlinear interaction of highly excited molecules near the dissociation limit.

Experiments on dissociation of SF_6 molecules by pumping its combination vibrations, $\nu_2 + \nu_6$ in particular, have shown that the dissociation threshold is essentially the same as for the ν_3 band although the intensity of $\nu_2 + \nu_6$ is approximately 100 times weaker than that of ν_3. This provides support for the statement above.
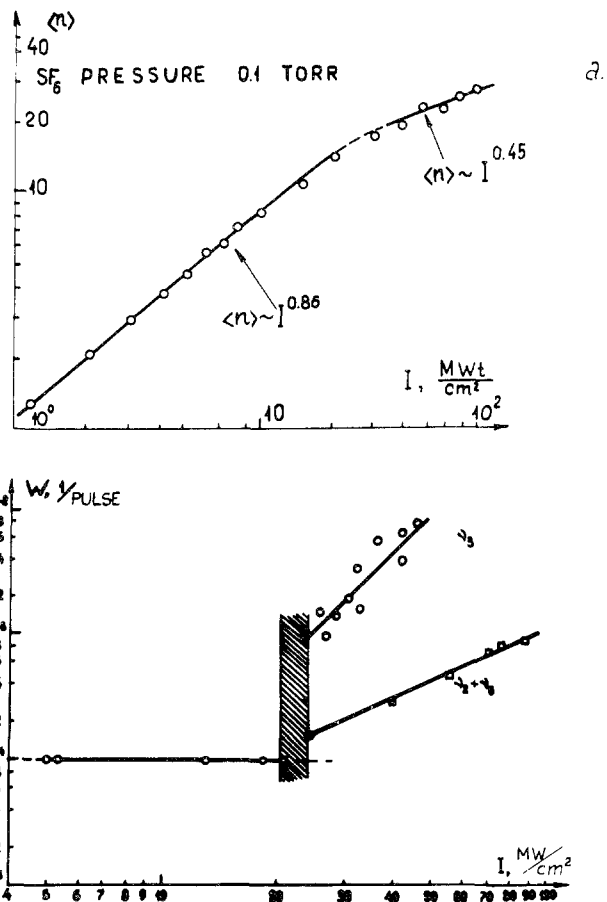

Figure 3. (a) Dependence of energy absorbed by one molecule of SF_6, expressed by the number of CO_2-laser radiation quanta $\langle n \rangle$, on incident power (pressure in the cell is 0.1 Torr, laser pulse duration is 90 ns). (b) Dependence of dissociation rate W on incident power. The threshold is independent of pressure in the range 0.05–0.5 Torr. Upper line is for pumping the ν_3 band in SF_6. Lower line is for pumping the $\nu_2 + \nu_6$ band in SF_6.

From the available experimental data, briefly stated above, an attempt has been made to find a theoretical explanation for the observed effects.

Explanation for the Process of Selective Dissociation

How does a polyatomic molecule absorb enough IR photons to dissociate into separate fragments, while simultaneously keeping the absorption resonant enough for isotopically selective dissociation to occur? Figure 4a shows how, in our opinion, this happens with SF_6 molecules.[26] Our explanation is based on a combination of the effect of "triple vibrational–rotational resonance" with the effect of nonresonance absorption at the transitions in the "vibrational quasi-continuum" of a polyatomic molecule.

The first three induced transitions of a molecule can be in exact resonance with the field, the frequency of which is tuned to the Q branch of the transition $v = 1 \rightarrow v = 2$. In spite of vibrational anharmonicity, this is achieved by compensation for the anharmonic shift of the transition energy by a shift in the opposite direction which results from a change in the rotational state. "Rotational compensation" for anharmonicity takes

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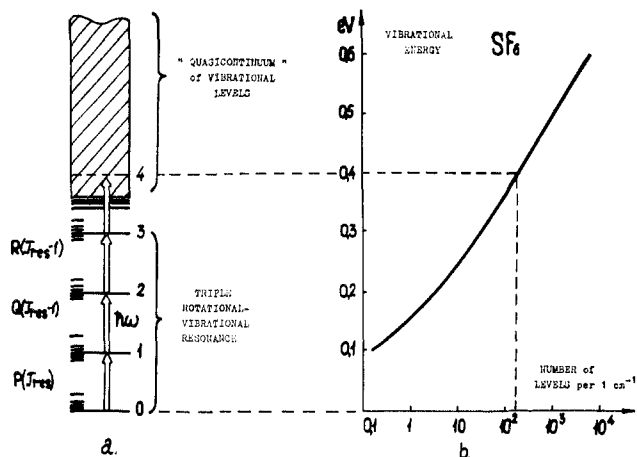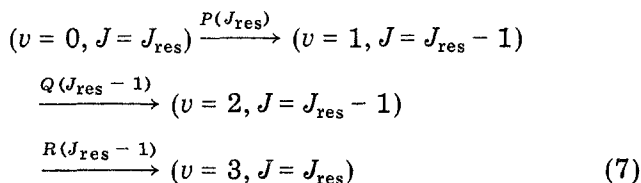
Figure 4. The possible interpretation of the molecule SF_6 selective dissociation by IR radiation based on the combination of two effects: (1) triple vibrational–rotational resonance which provides the selective excitation of level $v = 3$ in spite of vibrational anharmonicity, and (2) absorptions on the transitions in vibrational quasicontinuum which has rather high level density for molecule SF_6 beginning with the vibrational level $v = 4$. To the right the dependence between the density of vibrational levels of molecule SF_6 and the vibrational excitation energy is given.

place in three successive vibrational–rotational transitions of a molecule:

$$(v = 0, J = J_{res}) \xrightarrow{P(J_{res})} (v = 1, J = J_{res} - 1)$$

$$\xrightarrow{Q(J_{res} - 1)} (v = 2, J = J_{res} - 1)$$

$$\xrightarrow{R(J_{res} - 1)} (v = 3, J = J_{res}) \qquad (7)$$

This effect exists in polyatomic molecules for which the following conditions are fulfilled:

$$\Delta\nu_{anh} < \delta\nu_P, \delta\nu_R \qquad (8)$$

$$|\Delta\nu_{anh} - 2BJ_{res}| \gtrsim \Delta\nu_{P,br} \qquad (9)$$

where $\delta\nu_P$, $\delta\nu_R$ are the widths of P and R branches of a vibrational molecular band being excited, B is the rotational constant, $\Delta\nu_{P,br}$ is the molecular transition broadening by an intense field $\mathscr{E}$ expressed by

$$\Delta\nu_{P,br} = \frac{P_{v,v+1} \mathscr{E}}{2\pi\hbar c} \qquad (10)$$

and $P_{v,v+1}$ is the matrix element of the vibrational transition dipole moment. Under conditions 7 to 9 there always exists·a resonance rotational quantum number, J_{res}, for which the molecules in a comparatively moderate field with the intensity

$$I_{exc} \simeq \frac{\pi}{2} c \left(\frac{\hbar cB}{P_{v,v+1}} \right)^2 \qquad (11)$$

are directly excited to the third vibrational level. For a typical polyatomic molecule with $B \simeq 0.05$ cm^{-1} and average transition dipole moment $P_{v,v+1} \simeq 0.3$ D, the required intensity $I_{exc} \simeq 10^5$ W/cm^2. To excite very weak vibrational transitions with $P_{v,v+1} \simeq 0.03$ D we should have $I_{exc} \simeq 10^7$ W/cm^2.

For an excited polyatomic molecule an increase in the vibrational energy level density becomes essential. This is characteristic of any quantum system with many
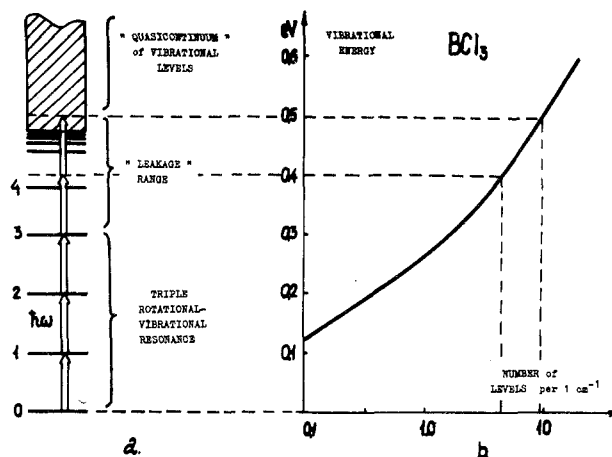

Figure 5. The possible interpretation of the molecule BCl_3 selective dissociation by IR radiation based on the combination of three effects: (1) triple vibrational–rotational resonance which provides the selective excitation of level $v = 3$; (2) two-photon transition $v = 3 \rightarrow v = 5$ with field-frequency detuning relative to intermediate level $v = 4$; (3) absorptions on the transitions in vibrational quasicontinuum which has rather high level density for molecule BCl_3 beginning with the vibrational level $v \simeq 5$–6 only. To the right the dependence between the density of vibrational levels of molecule BCl_3 and the vibrational excitation energy is given.

degrees of freedom where a certain excitation energy may be obtained through a great number of versions of its distribution between different degrees of freedom. For instance, in an atom where only one or at most two electrons are being excited this effect is absent. It is also absent in two- or three-atom molecules. But in a polyatomic molecule, begining with a certain vibrational energy, the density of vibrational levels increases so that they overlap one another and form a continuum of weak absorption far below the dissociation limit. Figure 4b shows the dependence of the vibrational level density on total energy G_0 in electron volts stored in a molecule, calculated from the formulas given by Haarhoff.[27] When the density of molecular vibrational levels $P(G_0)$ with energy $G_0 = 4\hbar\omega$ is rather high, for example

$$P^{-1}(G_0) \gtrsim \Delta\nu_{p,br} \qquad (12)$$

the molecules from the stage $v = 3$ can directly pass into the states of the vibrational "quasi-continuum" and then reach the dissociation limit within the ground electronic state (Figure 4a). It is just such a situation that takes place, in our opinion, in SF_6 molecules.

Since in the case of triple resonance high intensities are not required to excite the level $v = 3$, the dissociation threshold intensity depends on molecular excitation in the "quasi-continuum" which demands rather high densities of laser pulse energy (several J/cm^2 for SF_6) because of a small value of the absorption cross section. This accounts for the fact that the dissociation threshold intensity of SF_6 is independent of band intensities. The absorption band intensity has an influence only on the excitation intensity I_{exc} of the triple resonance transition, with its value remaining below the threshold intensity of dissociation in any case. The selective excitation of the level $v = 3$ at the expense of triple vibrational–rotational resonance may be also responsible for the shift in the frequency dependence

(27) P. C. Haarhoff, *Mol. Phys.*, **7**, 101 (1963).

of the dissociation rate by $\Delta\nu_{anh}$ since for triple resonance (eq 7) the laser frequency must be in resonance with the Q branch of the intermediate transition $v = 1 \rightarrow v = 2$.

The case when the limit of the vibrational quasi-continuum is rather low cannot be realized, of course, for many other molecules. For example (Figure 5), after a BCl_3 molecule absorbs three IR photons through the triple rotational–vibrational resonance, the density of vibrational levels is not enough yet for further automatic resonance with the monochromatic laser field. Here another effect appears, called the effect of molecular "leakage" into the vibrational quasi-continuum, even when the frequency of the intermediate transition $v = 3 \rightarrow v = 4$ is essentially detuned from the exact resonance with the IR field.[28] In essence, we deal here with the two-photon transition $v = 3 \rightarrow v = 5$ under conditions when the molecules do not accumulate at level $v = 5$ due to the induced transitions in the vibrational quasi-continuum. It looks like molecule "leakage" through the transitions $v = 3 \rightarrow v = 5$ at a rate less than the rate of molecules coming at level $v = 3$ and their leaving the level $v = 5$. With a radiation intensity of $10^8 \ W/cm^2$ in 10^{-8} s full leakage occurs with the detuning $|\omega - \omega_{34}| \simeq 5 \ cm^{-1}$. This mechanism employs, in principle, two-photon molecular transitions from the state $v = 3$ to $v = 5$.

In intense IR fields (10^7 to $10^9 \ W/cm^2$) two- and three-photon transitions even between lower vibrational levels may contribute, of course. In particular, due to the two-photon transition $v = 0 \rightarrow v = 2$, an excitation resonance is possible at a frequency between the transition frequencies ω_{01} and ω_{12}.[28] Similarly, due to the three-photon transition $v = 0 \rightarrow v = 3$ an excitation resonance may take place at a frequency between ω_{01} and ω_{23}, which may coincide with the Q branch of the intermediate transition $1 \rightarrow 2$.[29] The frequency of such a three-photon resonance exactly coincides with that of the triple rotational–vibrational resonance discussed above. There is an essential difference between these two types of resonance, however. In triple rotational–vibrational resonance, only molecules with a particular quantum number J_{res} may take part. Because of broadening, the process in a strong field may involve a considerable number of rotational levels, but in any case the portion of molecules dissociating during a short pulse, with no contribution by rotational relaxation, is limited by the value $\Delta\nu_{P,br}/\delta\nu_P$. Three-photon resonances occur simultaneously for molecules in almost all rotational states, because anharmonicity compensation is achieved by the different sign of the detunings ($\omega - \omega_{01}$) and ($\omega - \omega_{23}$) rather than by the contribution of rotational energy.

Recently we have managed to prove directly the mechanism of selective dissociation for SF_6 molecules based on the effects of triple rotational–vibrational resonance and the vibrational quasi-continuum. The experiment employed the idea of separate selective molecular excitation by a comparatively weak IR field tuned to the resonance frequency of the Q branch of the transition $1 \rightarrow 2$ and dissociation of excited molecules by a strong nonresonant field due to transitions in the vibrational quasi-continuum.[30]
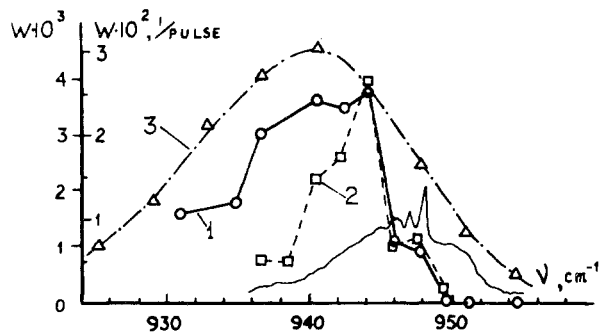

Figure 6. Dependence of dissociation rate of SF_6 molecules under two-frequency dissociation conditions on the excitation field frequency ω_1. The frequency ω_2 is fixed, $\omega_2 = 1080 \ cm^{-1}$, $I(\omega_1)$ = 4 MW/cm^2, $I(\omega_2)$ = 59 MW/cm^2; (a) at room temperature; (b) at 180 K; (c) analogous dependence for dissociation rate in a strong field, $I(\omega_1)$ = 60 MW/cm^2, $I(\omega_2)$ = 0.

Selective Dissociation in a Two-Frequency IR Field

As noted above, a molecule absorbs a large amount of energy in comparatively weak IR fields, and the intensity threshold of dissociation seems to be related to saturation of the vibrational transitions lying directly near the dissociation limit. It would be quite natural to separate the functions of selective excitation and dissociation between two fields with different frequencies. In this case we get a enhancement in selectivity since a nonresonant strong field does not cause power broadening of lower transitions and, on the other hand, to dissociate selective-excited molecules a strong field is required with rather broad tunability. Such a formulation of the problem is correct, of course, if the assumptions made in the previous paragraph are correct, at least qualitatively.

Below are given some results on the dissociation of SF_6 molecules by the field of two infrared frequencies ω_1 and ω_2.[30] The low-intensity field at ω_1 selectively excites the molecules and transfers the excited molecules to above the lowest boundary of the vibrational quasi-continuum. The frequency is in resonance with the molecular vibration ν_3. The field at ω_2 is tuned 130 cm^{-1} away from the absorption band of ν_3 and serves to excite the molecules in the quasi-continuum up to the dissociation limit. The frequency ω_2 and the intensities of both frequencies are selected so that the molecules of SF_6 in the reaction vessel dissociate only with both fields present.

Figure 6 presents some measurements of the frequency dependence of the dissociation rate in a two-frequency field when ω_1 is scanned. For comparison, the dissociation rate by a single-frequency intense field is also shown. It is seen from Figure 6 that in a two-frequency field there is no dissociation at all if ω_1 is tuned to the transition frequencies of SF_6 in the R branch, and molecules can dissociate only if the Q and P transitions are selectively excited. In addition, the resonance characteristic of W_i is narrowed here, leading to an increase of dissociation selectivity.

This experiment can be considered as direct evidence for the correctness of the qualitative mechanism for the dissociation of polyatomic molecules by intense IR radiation.

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Conclusion

The discovery of the effect of dissociation and excitation of high-lying vibrational states of polyatomic molecules by intense IR radiation has made it possible to investigate many hard-to-solve problems:

(1) Excitation of high vibrational levels with energies of several electron volts.[3] However, we have to devise some techniques for excitation of particular high vibrational levels without distributing the molecules over many vibrational levels. In principle, it is possible to solve this problem by combining the effects of triple rotational–vibrational resonance in comparatively weak fields with the influence of very strong IR pulses on excited molecules.

(2) Investigation of spontaneous transitions between highly excited vibrational states, in particular, collision-less intramolecular v–v relaxation. The first successful experiments of the kind have been conducted on OsO_4 molecules.[31]

(3) The studies of transition paths between the vibrational levels higher than $v = 1$. The PQR transitions discussed above are, of course, the simplest transition of this type, and to get a full picture of the transitions one needs further theoretical investigations.

The investigation of stimulated transitions between highly excited vibrational levels makes it possible to obtain information about the absorption coefficients, transition cross sections, and level densities in the "vibrational quasi-continuum". The action of a two-frequency IR field on molecules is a standard method of such measurements.

(4) Excitation of molecular electronic states due to transfer of the vibrational energy of highly excited molecules in the ground electronic state to the energy of electronic excitation (V–E process) and further increase of molecular vibrational energy caused by stimulated transitions in the vibrational quasi-continuum of an excited electronic state and molecular absorption of energy which is much higher than that of molecular dissociation.

(5) Investigations of the ways how bonds are broken in polyatomics in strong IR fields and the composition of resultant fragments (the first experiments on IR photolysis show that its products differ essentially from those of UV photolysis)[32] and search for cases of dissociation into saturated simple molecules which are characterized by high selectivity of secondary photochemical processes. The full information about these processes can be obtained in experiments on molecular beams and from probing molecular fragments by laser radiation, as has been lately done on NH_3 molecules[33] and C_2H_4 molecules.[34]

(6) Study of other unimolecular processes with highly vibrationally excited molecules, in particular, the process of isomerization. Successful experiments on the trans–cis transition of $C_2H_2Cl_2$ molecules have been performed.[35]

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Concentration of Solutes from Aqueous Solution

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Received September 15, 1976

Drinking water is commonly analyzed for biological organisms, hardness, pH, etc., but until recently little has been known about soluble organic material in water. Organic contaminants can impart a bad taste and odor to water. The effect of organic impurities on health is largely unknown, although a statistical link with incidence of cancer has been established for New Orleans water.[1] There is considerable interest in establishing what organic contaminants are actually present in various drinking water samples and in looking for ways to improve the quality of our drinking water with regard to organic impurities.

Analysis of waste water effluents for organic compounds is vital if industries are to meet environmental standards. There is also considerable interest in determining organic compounds in other types of aqueous samples. Groups such as those of Zlatkis at Houston[2]

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