

Multiphoton Dissociation in Molecular Beams

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Multiphoton dissociation in molecules has become a field of major significance during the past decade¹) after the early discovery of Isenor of a fast dissociation process occurring in SiF₄ gas in a low-pressure sample irradiated with intense CO₂ laser pulses. Experimental and theoretical studies were driven by the possibility of selective chemistry; laser isotope separation was soon demonstrated. It was a surprising effect because it did not fit the established theoretical picture of how molecules can absorb radiation. Theories on the coherent absorption of two photons in atoms, for which there came abundant experimental verification in the early seventies, predicted that even if not necessary for the event, the presence of a quasi-resonant intermediate state increased

by orders of magnitude the two photon transition probability which was also dependent on the square of irradiation intensity. In the case of molecules, the number of infrared photons that need to be absorbed in order to raise the energy of excitation close to the dissociation threshold greatly exceeded twenty, so that the cross-section for the resonant absorption of such a number in view of the anharmonicity of molecular vibration, should be vanishingly small.

Early experiments showed that, in practice, dissociation was reached at moderate intensities (of the order of 30 MW/cm²) so that interaction time was also playing an important role in the dissociation. However the notion that the process could be described by a series of step-wise incoherent one photon transi-

Fig. 2 — Schematic of molecular beam apparatus for two frequency IR multiphoton dissociation. At the bottom, the nozzle-skimmer region is sketched: (a) gas reservoir, (b) free jet region, (c) molecular beam region.

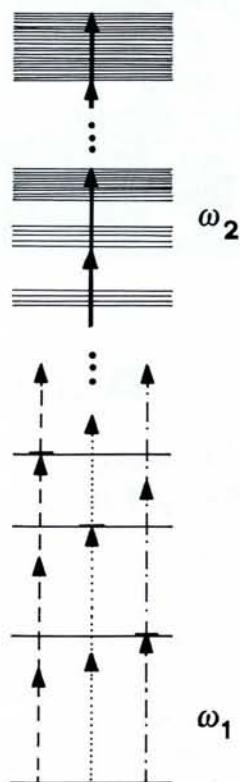
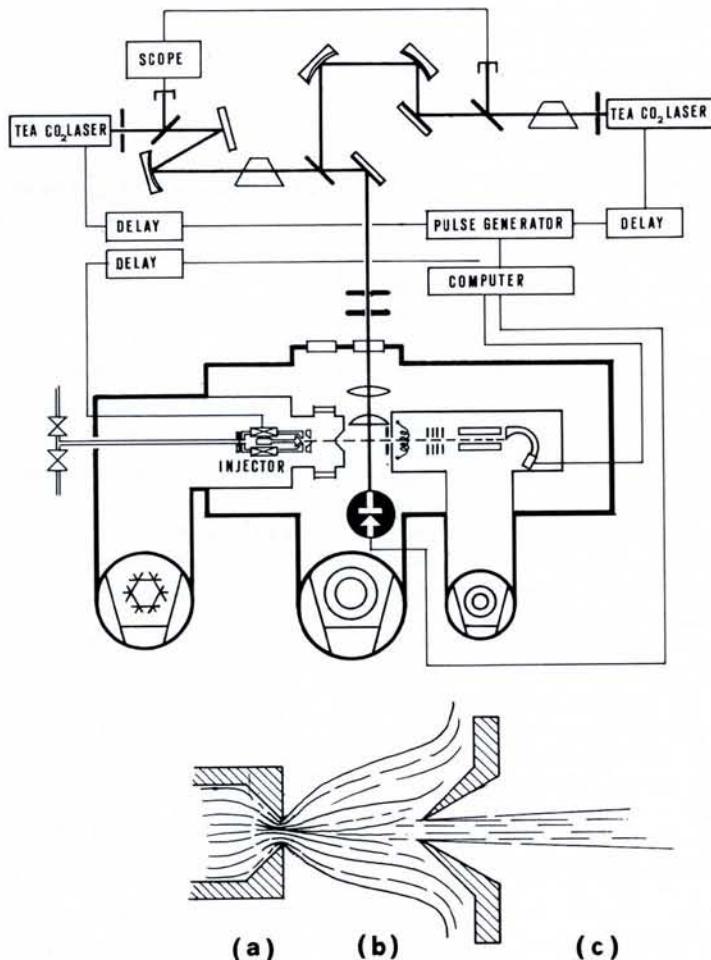


Fig. 1 — Model for one and two frequency IR multiphoton excitation. In the discrete level, a one-photon resonance is schematized with dotted-dashed arrows, a two photon resonance with dotted arrows, a three photon with dashed arrows.

tions over a set of equally spaced energy levels, (so explaining dissociation as a unimolecular reaction following the usual chemical kinetic equations) could not account for the isotopic selectivity of the process.

Dynamics of Multiphoton Excitation and Dissociation

The conventional model of multiphoton excitation and dissociation (MPE and MPD) divides the vibrational states of a molecule undergoing this process into three distinct regions of increasing energy (Fig. 1), corresponding to a sparse spectrum at low energies (the so-called discrete region), a dense spectrum of discrete molecular eigenstates below the dissociation threshold (the so-called quasi-continuum) and a true continuum above the threshold. The vibrorotational states of a polyatomic molecule in the regions below the continuum can be represented as a single lower level and successively higher bands of closely spaced levels. These bands are related to molecular structure.

In the discrete region, the laser radiation is absorbed coherently and the Schrödinger equation properly describes the dynamics of the process. A characteristic feature of this quantum mechanical description is the occurrence of

multiphoton resonances, that is direct transitions from one band to a non-neighbouring band by the absorption of more than one laser photon when the laser frequency ω_L is equal to $1/N$ of the energy difference between the ground and the excited state with N vibrational quanta: $\omega_L = 1/N(\varepsilon_N - \varepsilon_0)$. The resulting absorption cross-section is proportional to the N_{th} power of laser intensity and inversely proportional to the product of intermediate detunings. The width of the resonances tends to decrease with the order of the resonance.

In principle, multiphoton excitation should be described by the Schrödinger equation also in the quasi-continuum. But as the level of excitation increases, the spectral congestion becomes very high and the density of states is such that practical considerations may prevent our using the coherent description. Multiphoton excitation in the quasi-continuum has been described most often by rate equations for the populations of the vibrational states. While the fundamental validity of rate equations in the quasi-continuum remains in doubt, since it does not predict the occurrence of structure at high levels of excitation, this approach has been somewhat successful in modelling the total energy absorbed during the process.

In the continuum region, the energy is randomized between molecular modes and unimolecular reaction rate theories can account for the process. The dissociation cross-section becomes proportional only to the laser fluence ($I \times t$) and no structure is predicted in this region. This implies that differences in absorption in the discrete region are mainly responsible for isotopic selectivity.

Basic Molecular Beam Techniques for Multiphoton Processes

Supersonic molecular beams have recently become widely used for spectroscopic applications. They offer the possibility of performing experiments in a collisionless regime at a selected and well defined rotovibrational temperature. Moreover parameters can easily be varied by changing source pressure and temperature.

Although supersonic expansion was well known in the world of engineering, the application of this knowledge to molecular beams for the study of chemical kinetics by Kantrowits and Gray started only in the early fifties to be further developed by Anderson and Fenn²⁾. As is schematically shown in Fig. 2, in order to form a supersonic free jet, two differentially pumped sections, a reservoir (a) and an expansion chamber (b),

separated by a nozzle are necessary. A third chamber (c) can be added if the free jet is to be collimated by passing through a cone-shaped orifice called a skimmer. The molecules contained in the reservoir at high pressure, usually mixed with a carrier rare gas, expand in a continuous flow near the nozzle and become vibrorotationally cooled, because of the collisions which allow the transformation of their internal energy into kinetic energy with the vector velocity peaked forwards. Downstream there is a transition from continuous to molecular flow where the mean free path is long and after that there is a beam stopper (Mach disk). Translational and rotational temperatures of the order of a few kelvin can be reached in supersonic expansion. Rotational and vibrational temperatures are measured through IR high resolution diode laser spectroscopy, or by Raman spectroscopy using a visible laser focussed onto the beam as the excitation source. Multiphoton excitation can be studied both in the free jet zone where the molecular density is very high (≈ 10 torr) or in the molecular beam zone where the density is low and collision free experiments can be performed. A suitable device to monitor multiphoton

absorption in a molecular beam is the bolometer based on optothermal detection.

Experiments in the molecular beam with this device have been performed with a line-tunable CO₂ laser for SF₆ and CF₃Br molecules^{1c)}. Results for CF₃Br are in agreement with non-linear spectroscopy data obtained in our laboratory in an optoacoustic cell using a continuously tunable CO₂ laser^{1b)}. The multiphoton dissociation yield can be measured in real time by a mass spectrometer in two different ways: either monitoring on-line the decrease of the primary beam intensity due to recoil of fragments after dissociation, or detecting fragments at different angles with respect to the molecular beam axis. A typical apparatus for multiphoton dissociation, which has been built in Frascati is shown in Fig. 2.

Multiphoton Dissociation Results

The one-frequency experiments performed at an early stage by Y. Lee's group in Berkeley³⁾ gave information on the overall character of the process only and mainly demonstrated that dissociation was obeying unimolecular dynamics. Both the line-tunable lasers used and the high fluences needed to detect

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appreciable dissociation hid the structural features.

The use of more than one frequency has given insight at the microscopic level into each step of the excitation process. In such experiments, a first laser of moderate intensity excites the molecules in the discrete region, while a second, more powerful laser brings the excited molecules up and beyond the dissociation threshold. By varying the frequency ω_1 of the first laser around the absorption band, while keeping the frequency ω_2 of the second laser fixed, characteristic features of coherently excited low level transitions can be exploited. The quasi-continuum region can be studied by varying the frequency of the second laser ω_2 when ω_1 is tuned near to the absorption maximum.

Excitation in the First Discrete Levels

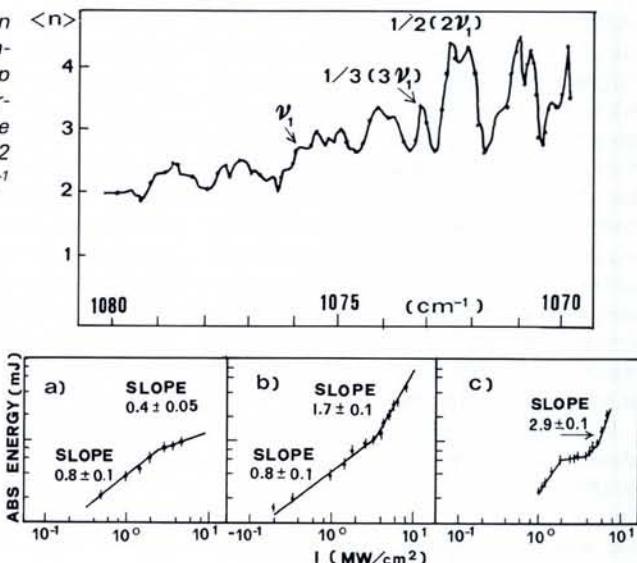
When two-frequency molecular beam dissociation measurements were first made using line-tunable lasers (by Y. Lee on SF_6 ³⁾) to investigate excitation in the discrete levels, fine structures in the excitation spectrum could not be seen — only an overall narrowing of the shape. In contrast, a very rich structure was found with free jet expansion when a continuously tunable CO_2 laser was used as a first stage of excitation⁴). Some of these structures can be interpreted in terms of coherent multiphoton transitions between discrete levels.

It should be noted that narrow resonances like those found in the SF_6 excitation spectrum are of great practical importance since they can provide pathways for high isotopic selectivity in the dissociation of heavy polyatomic molecules with a small isotopic shift. Such resonances have been observed in several molecules of different symmetry in our laboratory and the absorption spectra of SiH_4 , CF_3Br , CF_3I and C_2F_5Cl measured at room temperature. Structures have been assigned as multiphoton resonances from their wavenumber position and laser intensity dependence at different wavenumbers. This has allowed us to identify in the case CF_3I , resonances up to the $N = 3$ order as shown in Fig. 3.

Excitation in the Quasi-continuum

Due to the difficulties of modelling the excitation through highly excited vibrational levels, it is of great importance to investigate the nature of the quasi-continuum. This has been accomplished for several molecules, e.g. SF_6 , SiF_4 , CF_3Br , C_2F_5Cl , in a collision free regime with the two frequency apparatus shown in Fig. 2.

Fig. 3 — CF_3I multiphoton absorption spectrum measured at $\phi = 0.16 \text{ J/cm}^2$, $p = 0.1 \text{ Torr}$. Absorbed energy versus laser fluence measured at $\omega = 1075.2 \text{ cm}^{-1}$ (a), $\omega = 1072.6 \text{ cm}^{-1}$ (b), $\omega = 1073.3 \text{ cm}^{-1}$ (c).



Strong spectral features in the quasi-continuum of a multiphoton excited molecule were first deduced from the dependence of the C_2F_5Cl dissociation yield on the frequency of the second laser^{1b}). The close correlation between the multiphoton dissociation spectra and linear spectroscopy data suggests that intensity borrowing by combination bands that lie near the infrared active fundamental levels may be responsible for this structure.

Results obtained in a two frequency molecular beam dissociation experiment, on CF_3Br ^{1b}), are presented in Fig. 4. To achieve a low rotational temperature so that only pure vibrational multiphoton resonances play a dominant role, CF_3Br was expanded in a 10% argon seeded beam. In spite of using line-tunable lasers, a remarkable structure was observed. In the wavenumber region closest to the ν_1 resonant absorption ($\omega_2 > 1050 \text{ cm}^{-1}$), peaks are

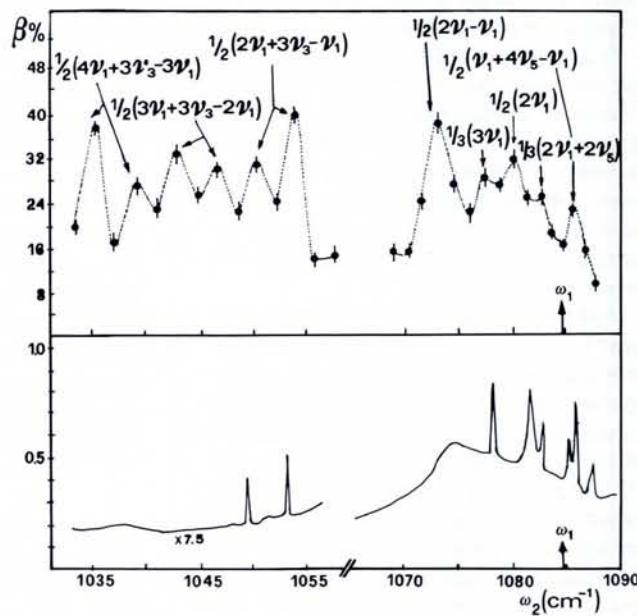
mainly related to the discrete region with resonant excitation of two or three quanta. The intense red shifted peaks can be explained only in terms of a structured quasi-continuum, as in the case of C_2F_5Cl . Calculations that take account of ν_1 , $2\nu_5$, $3\nu_3$ modes and their combination up to the fourth level, confirm this hypothesis, whereas those based only on statistical theories predict a featureless dissociation peaked near the ν_1 mode absorption.

Excitation in the Continuum

At variance with the case of the quasi-continuum, our present knowledge of processes occurring in the continuum appears to be almost complete and manageable models are available.

As already pointed out, most of the population is brought to the continuum only at very high laser fluences where power broadening implies that only a broad convolution of resonances can ap-

Fig. 4 — CF_3Br two frequency multiphoton dissociation spectrum measured in a 10% Ar seeded supersonic beam; $\omega_1 = 1084.64 \text{ cm}^{-1}$, $\phi_1 = 1.5 \text{ J/cm}^2$, $\phi_2 = 3.5 \text{ J/cm}^2$. Data are compared with the calculated spectrum shown below.



pear in the spectrum. This was clearly observed in Y. Lee's laboratory where a detailed investigation of the role played by both fluence and intensity at very high levels of excitation was performed on several molecules (e.g. SF₆, CF₃Cl, N₂ N₄) having different densities of states close to the continuum region³). In some cases (e.g. C₂F₅Cl) the average level of excitation can overcome more than one dissociation channel, so that the molecule can dissociate into different products. Experiments where the angular distribution and translational energy of the fragments were determined, have provided a check on the validity of statistical theories in the continuum, i.e. to study the redistribution of energy occurring there under unimolecular dissociation, the fragmentation process and the energy retained in each fragment. The main results are:

dissociation yield depends only on laser fluence, but the average level of excitation reached still depends on laser intensity; a large molecule is easily dissociated and acquires more energy than a small molecule at the same laser fluence. Most of the excess energy is retained as excitation energy in the fragments.

These conclusions seem to confirm the validity of the statistical theory describing IR multiphoton dissociation of most of the polyatomic molecules excited by conventional CO₂ lasers (≈ 100 ns pulse duration). The dependence on intensity of the average level of excitation reached above the dissociation threshold has left some hope for a practicable bond-selective photochemistry in the future, provided that very short (10-100 ps) and intense IR laser sources become available.

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Theory of Energetic Ion-Atom Collisions

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The theory of ion-atom collisions concerns the calculation of the atomic states resulting from the collision between two nuclei and their attendant electrons. Although the existence of nuclear resonances occasionally may play an interesting role, it is usually adequate, at the energies which are relevant to atomic physics, to consider all particles to interact only via the electromagnetic interaction and the nuclei to remain intact throughout the collision. The Hamiltonian governing the motion of the interacting atoms is known, and it is only a matter of solving the time-dependent Schrödinger equation or the equivalent equations of the time-independent formulation of scattering theory to calculate the probabilities of transition into the various excitation, break-up, or rearrangement channels which are energetically available.

From this point of view, it is quite natural to question the pertinence of further effort in this field. Most collision experiments in nuclear and particle physics have the ultimate aim of deducing the forces between the constituent particles. What then is to be learned from atomic-collision experiments? After all, there is not much need to test the validity of the time-dependent Schrödinger equation for nonrelativistic motion.

Nevertheless, aside from the enormous technological and astrophysical applications, the field of atomic collisions is of considerable fundamental interest. It is precisely the exact knowledge of the forces of interaction that allows a sensitive test of collision theory to be made, a possibility not so easily open to nuclear and particle theorists. Any theory of such collisions must rely on approximation procedures or model assumptions. Because of this, it is essential that the atomic interaction forces are known exactly so that the modelling of specific collision-dynamic features may be exposed to a unique test.

At first sight, it may seem that atomic-collision theory is simplified by the simple mathematical form of the static Coulomb interaction, which for most purposes can be considered to be dominant. Unfortunately, the infinite range and other peculiarities of the Coulomb force endow the theory of atomic colli-

sions with a fundamental delicacy and invalidate most theorems and rigorous formulations applicable to short-range forces. Indeed, the standard methods of scattering theory are not applicable unless the interaction amongst asymptotic channels decays faster than the Coulomb interaction. Much effort is still devoted to the resolution of this fundamental problem, but a complete clarification has not yet emerged.

The problem is usually circumvented by arguing that it is acceptable to assume that Coulomb interactions are cut off or appropriately screened at distances extremely large on the atomic scale. After all, particle detectors are not set up in the laboratory infinitely separated from the scattering chamber. Then it is physically sound to expect that the description of specific processes occurring on the atomic scale will be independent of the details of the screening procedure if the screening radius is made sufficiently large. There is no evidence that this supposition is invalid, but it is essential to exert particular care to ensure complete consistency if difficulties with irregularities in the limit of a pure unscreened Coulomb force are to be avoided. Accordingly, we believe that ordinary formal scattering theory may be applied in atomic collisions if one is sufficiently careful, as seen in Panel 1.

The effect of an atomic collision is either to excite one or more electrons of either target or projectile to bound states, to transfer electrons from bound states around one nucleus to bound states around the other (electron capture), or to eject electrons into the continuum (ionization). Electron excitation and electron capture are uniquely defined as single-channel and rearrangement-channel processes, respectively. The situation is not so clear in the case of ionization. In principle, ionization is a break-up process, but it is convenient to talk about target ionization if the ejected electron is relatively slow with respect to the residual target ion and about capture to the projectile continuum if the ejected electron is slow with respect to the projectile. This distinction merely reflects the consideration that target ionization may be understood in a single-channel approach, while capture to continuum requires a rearrangement-chan-