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DYNAMICS OF EXCITATION AND REACTIONS OF SIMPLE MOLECULES INDUCED BY LASER RADIATION

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ABSTRACT

The process of multiple photon excitation and dissociation of polyatomic molecules by I.R. laser radiation is reviewed.

Results on molecules of different symmetry in the discrete, quasi-continuum and continuum regions are presented and discussed.

INTRODUCTION

Multiple photon excitation and reactions of simple molecules induced by IR laser radiation has become a field of major significance during the past decade in view of the possibility offered to selective chemistry and laser isotope separation. In particular for what concernes laser isotope separation, the interest was raised by the demonstration of isotopic slectivity in the multiple photon dissociation of SF_6 /1/, which has been shown to occur in absence of collisions. An analogous dissociation process had been previously observed in another molecule, SiF_4, in a low pressure sample irradiated with intense CO_2 laser pulses /2/.

Observation of this phenomenon was only possible with the high intensities typical of lasers. It was a surprising effect because did not fit the established theoretical picture of how molecules can absorbe radiation. In fact on one side the availability of lasers in the visible region of frequencies in the early seventies led to abundant experimental verifications of 1931 pioneering work of Goeppert Mayer /3/ of coherent absorption of two photons in atoms. The theory predicted that even if not necessary for the event, the presence of a quasi resonant intermediate state led to an increase of orders of magnitude in the two photon transition probability having an intensity dependence of the order of two. On the other side, in case of molecules, the number of CO_2 laser IR photons to be absorbed in order to raise the energy of excitation close to the dissociation threshold strongly exceeded twenty so that resonant absorption of more than 20 photons, in view of the anharmonicity of any molecular vibration, should lead to a vanishingly small cross section.

Early experiments showed instead that the dissociation was reached at moderate intensities (of the order of 30 MW/cm^2) and that also fluence was playing an important role in the dissociation. However the assumption that this process could be described only by step-wise incoherent one photon transition among a set of equally spaced energy levels, so explaining dissociation as unimolecular reaction following usual chemical kinetic equations is also unadequate to account for the isotopic selectivity of the process.

A satisfactory theoretical model should account on one side for coherent interaction of the laser radiation with low lying molecular levels as well on the otherside for incoherent absorption of radiation in the upper levels as the dissociation threshold is approached and overcome.

A series of experiments has been performed in our laboratory to identify a suitable model in describing multiphoton processes. In particular we have studied molecules whose absorption spectrum matches the emission lines of CO_2 laser radiation and which belong to different symmetry groups.

DYNAMICS OF MULTIPHOTON EXCITATION AND DISSOCIATION.

The conventional model of multiphoton excitation and dissociation /4/ divides the vibrational states of a molecule undergoing this process into three distinct regions of increasing energy 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 dissociation.

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 particular in highly symmetric molecules anharmonic splitting of the degenerate excited states and Coriolis splitting as well as rotational states are responsible for the band shape, while in asymmetric molecules the same role is played by the presence of normal modes almost degenerate with combination tones and overtones as well as the rotational manifold.

In the discrete region the laser radiation is absorbed coherently and Schroedinger 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 neighboring 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: $\omega_L = 1/N\ (\varepsilon_N - \varepsilon_o)$. The absorption cross section results proportional to the N power of laser intensity and inversely proportional to the product of intermediate detunings. The width of the resonances tend to decrease with the order of the resonance.

In principle multiphoton excitation should be described by 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 consideration may prevent to use 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 modeling the total energy absorbed during the process.

In the continuum region randomization of energy between the molecular modes is accomplished and unimolecular reaction rate theories can account for the dissociation process. The dissociation cross section becomes proportional only to the laser fluence (I×t) and structures are not predicted in this region. From this description it comes out that absorption in discrete region is the main responsible for isotopic selectivity, which can only be kept going through the other two regions.

EXPERIMENTAL AND RESULTS

In our laboratory, a series of studies have been done in order to ascertain the validity of this model. Experiments were performed in all the three above mentioned regions by use of different sophisticated techniques to reveal multiphoton excitation and dissociation of molecules in the gaseous phase. In what follows techniques and experimental procedures as well as results will be reported and discussed.

a) Experiments in the discrete region

Evidence of the existence of multiphoton resonances has been searched on molecules of different symmetry in order to investigate how the mechanism to overcome the anharmonicity barrier works. In case of spherical top molecules the anharmonicity of energy levels is compensated by the vibrational anharmonic splitting which occurs in the exicted states of the resonant degenerate mode of vibration and Coriolis splitting. The anharmonic splitting of the states of the pumped mode and the rotational structure of each level increase the number of multiphoton resonances so that at room temperature a nearly continuous excitation spectrum is expected except for molecules having a high rotational constant B.

In case of symmetric tops and asymmetric molecules the interaction among the levels of the pumped mode (generally non degenerate) with combination bands helps in overcoming the anharmonicity barrier. A relevant spectral structure due to vibrorotational multiphoton resonances in the first discrete steps is expected in the multiphoton absorption (MPA) spectra. As significant examples, in the following we show results obtained on a symmetric top molecule (CF_3I) and on a spherical top with high B (SiH_4).

Experiments were performed with the multiphoton I.R. spectrometer assembled in Frascati, which is shown in Fig. 1 /5/. It consists of a continuously tunable high pressure (10 atm) CO_2 laser (Δv = 0.12 cm^{-1}) whose frequency is varied in the range 9-10 μm by a stepping motor mounted on the grating and an optoacustic cell detector. In the skematic of the apparatus, the electronic data processing and computer control of laser energy and wavelength are shown. By use of this apparatus narrow resonances have been observed in the MPA spectra of symmetric and asymmetric tops /5/; while the same experiments performed with a line tunable CO_2 laser revealed only a broad structure. In Fig. 2, the MPA spectrum of CF_3I taken at two different temperatures is shown (p = 0.1 torr; ϕ = 0.11 J/cm^2). Peaks were tentatively assigned on the basis of their frequency position and fluence and temperature dependence. Resonances are expected whenever the laser frequency is equal to 1/N of the energy difference between the ground and the excited state with N vibrational quanta. The energy levels of CF_3I have been calculated by use of the usual formula for symmetric tops /6/:

$$\varepsilon(v_1, v_2, \ldots\ldots v_6) = \sum_{i=1}^{6} (v_i v_i + \chi_{ii}\, v_i\, (v_i - 1) + \sum_{j>i} \chi_{ij} v_i v_j) + Bj(j+1) \tag{1}$$

in which known spectroscopic parameters have been inserted /7/. Calculations take into account interaction between v_1 and $2v_5$ mode as well as between v_1 and $v_2 + v_3$. Hot bands involving v_6 and v_3 as starting levels have been considered too. Calculations have been performed ignoring the distribution over the rotational states and considering all the molecules to start in the state with $J_0 = J_{max}$, where J_{max} is the quantum number corresponding to the maximum of the thermal rotational distribution. Prominent structures in the spectra are expected at the corresponding laser frequencies. The predicted positions of multiphoton resonances (shown on the lower lower abscissa) agree reasonably well with the experimental peaks. In order to confirm this assignement we have performed a MPA spectrum of CF_3I at low temperature (- 50° C). In fact, on the basis of (1) we expect the multiphoton resonances involving $j_f \neq j_{max}$ to shift with the maximum of the rotational distribution of the initial state as the gas temperature is decreased (j_{max} = 45 at room temperature and j_{max} = 34 at T = -50°C). The experimental MPA spectrum taken at -50°C show changes in the spectral features which can be reasonably explained by the previously mentioned temperature effect (horizontal arrows in the lower abscissa of Fig. 2(a) mark the predicted shift due to cooling of the gas). The assignment of spectral structures as multiphoton resonances has been tested through the behaviour of predicted one, two and three photon resonances in the ν_1 mode as a function of laser fluence (Fig. 2b). A linear dependence followed by saturation has been found for the one-photon peak, while the expected I^N behaviour has been found for N-photon resonances at high laser fluence.

Analogous results have been obtained in the MPA studies of CF_3Br molecule /5/ not reported here for sake of brevity.

As an example of spherical top molecule, preliminary data on MPA of SiH_4 are discussed. A portion of the absorption spectrum of SiH_4 measured with the continuously tunable CO_2 laser at $\phi = 0.07$ j/cm^2 and $\phi = 0.16$ j/cm^2 is reported in Fig. 3. Numbers mark one frequency resonances (linear absorption) assigned on the basis of positions and intensities /8/. Some new features (labelled with capital letters) appear clearly overimposed to the linear spectrum at low fluence. In order to ascertain the non linearity of the process which gives origin to the new structures, the spectrum has been measured also at high fluence ($\phi = 0.16$j/cm^2). In this case, multiphoton resonances appear to dominate the spectrum. Anyway, a better knowledge of the excited state spectroscopy of SiH_4 is necessary in order to fully assign the MPE spectra and clarify the mechanism of laser excitation.

b) Experiments in the quasi-continuum

Due to the difficulties in modelling the excitation through highly excited vibrational levels, it is of great importance to investigate the nature of the quasi-continuum. This study has been accomplished an several molecules, e.g. SF_6 /9/, SiF_4, CF_3Br /10/, $C_2F_5C\ell$ /11/, in collision free regime with an apparatus which consists of an expansion cooled pulsed molecular beam and a quadrupole mass spectrometer at forward angle with respect to the beam. Radiation from two TEA line tunable lasers can interact with the molecules, in a small 2 mm x 10 mm region, and laser induced MPD is monitored through the decrease of the primary beam intensity. With this apparatus a strong spectral structure in the quasi-continuum of a multiphoton excited molecule has been evidenced through the dependence of $C_2F_5C\ell$ dissociation yield on the frequency of the second laser /11/. The close correlation between the multiphoton dissociation spectra and linear spectroscopy data suggests that the intensity borrowing by combination bands that lie near infrared active fundamentals may be responsbile for this structure.

In order to demonstrate how much this kind of experiments contribute to the understanding of the dynamics of dissociation processes results obtained in a two frequency molecular beam dissociation experiments on CF_3Br molecule, 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 espanded in a 90% Argon seeded beam. In spite of the use of line tunable lasers, the two frequency technique at moderate laser fluences allowed to observe a remarkable structure. In the wavenumber region closest to ν_1 resonant absorption ($\omega_2 > 1050$ 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 considering a structural quasi-continuum, as in case of $C_2F_5C\ell$. Their absence in the spectrum calculated including ν_1, $2\nu_5$, $3\nu_3$ modes and their combinations up to the fourth level, confirm this hypotesis. These calculations have been performed by solving Bloch equations for the first four discrete levels and rate equations for the q.c. states /10/. On the other side calculations based on statistical theories predict a non structured dissociation peaked near the ν_1 absorption frequency.

In conclusions, in case of suitable systems, at moderate laser fluences and low rotational temperatures it was possible to demonstrate the occurrence of pure vibrational resonances in the discrete region and to reveal a rich structure in the quasi-continuum. The pumping of resonances, especially of the ones from pre-excited states permits to largely increase the selective dissociation yield as demonstrated in our laboratory in ^{13}C isotopic enrichment from CF_3Br in recirculating flow experiments /12/.

c) Experiments in the continuum

At variance with the case of the quasi-continuum, our present knowledge of processes occurring in the continuum like multiple photon dissociation (MPD) appears to be almost complete and manegeable models are available to describe them. As already pointed out, most of the population is brougth to the continuum only at very high laser fluences. The power broadening is such that only a broad convolution of resonances appear in the spectra. In some cases (e.g. $C_2F_5C\ell$ /13/) the average level of excitation can overcome more than one dissociation channel, so that the molecule can dissociate giving different products. Experiments performed by Y. Lee group /14/ seem to confirm the validity of the statistical theory in describe IR multiphoton dissociation of most of the polyatomic molecules excited by conventional CO_2 lasers (~ 100 nsec pulse duration). The dependence on intensity of the average level of excitation reached above the dissociation threshold has left some hopes of a bond selective photochemistry, provided that very short (10-100 psec) and intense IR laser sources are available.

CONCLUSIONS

From the above mentioned and discussed results as well by other obtained in our and other laboratories active in the field it can be concluded that multiphoton resonances play a major role in multiple photon excitation of the low lying vibrational states. In particular two photon resonances appear to dominate also the dissociation spectrum at moderate laser fluences. This fact can have some important consequences for laser chemistry and isotope separation. Higher selectivity can be achived in laser isotope separation as shown in case of CF_3Br /12/, through the excitation of multiphoton rather than single photon resonances. In laser photochemistry and in particular in laser vapor deposition /15/ efficiency could be enhanced through the excitation of two photon rather than one photon resonances. Work is in progress in our laboratory along these lines.

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Figure Captions

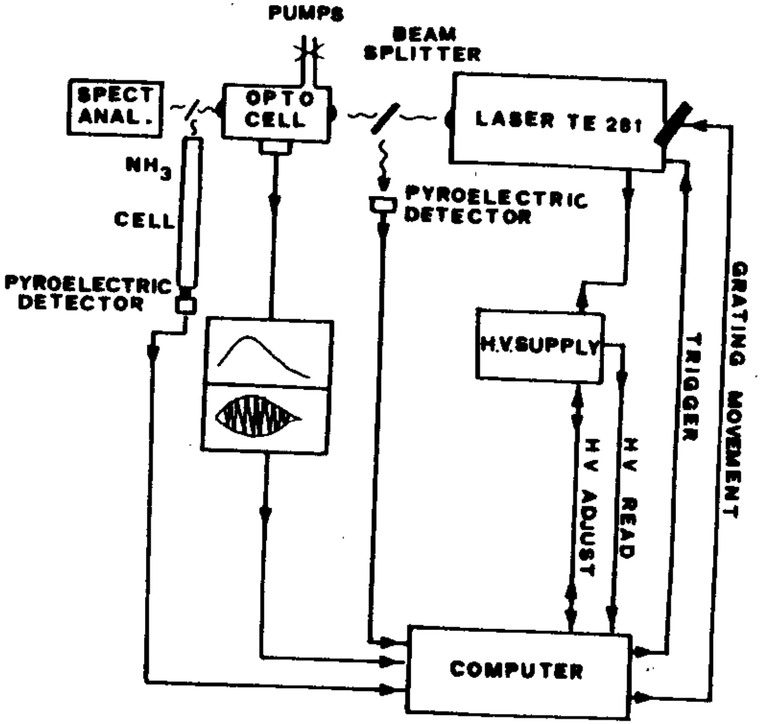
Fig. 1 Skematic of the multiphoton I.R. spectrometer

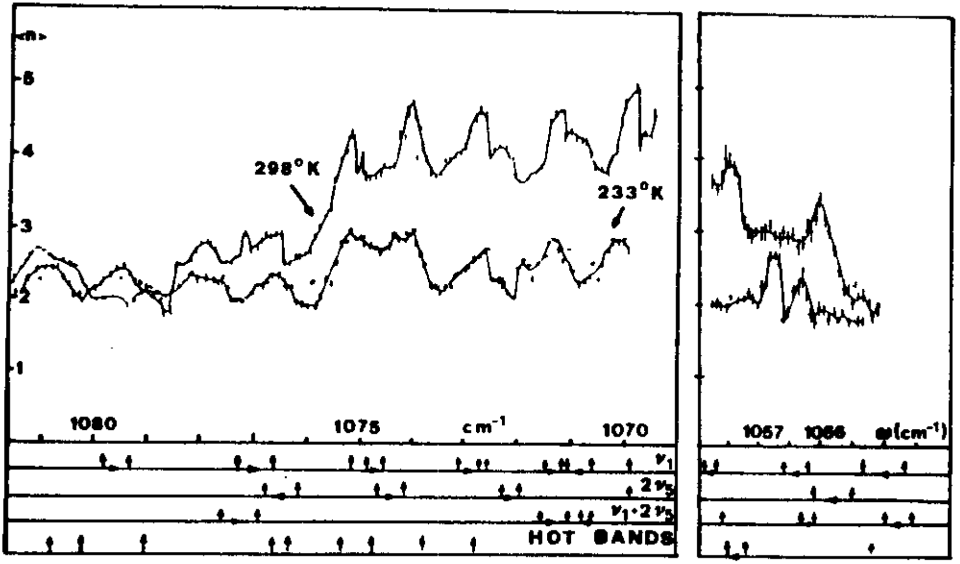
Fig. 2 a) MPA spectrum of CF_3I ($p = 0.1$ torr, $\phi = 0.11$ j/cm^2) at $T = 298$ K and $T = 243$ K

b) MPA of CF_3I versus laser fluence at three different excitation frequencies ($\omega_1 = 1075.2$ cm^{-1}; $\omega_2 = 1072.6$ cm^{-1}; $\omega_3 = 1073.3$ cm^{-1})

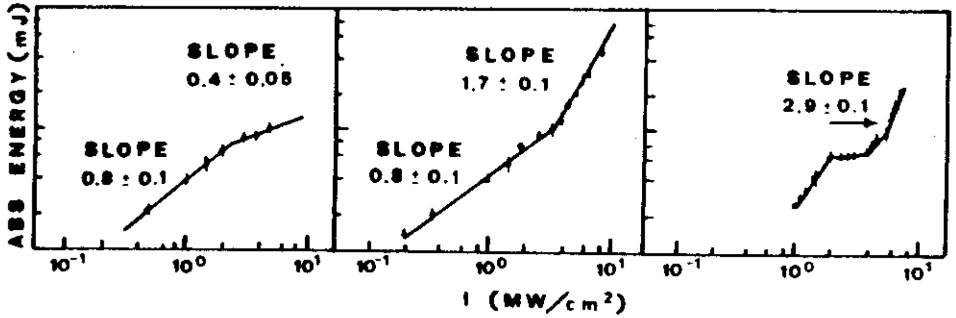
Fig. 3 MPA spectrum of SiH_4 at two different laser fluences; (a): $\phi = 0.07$ j/cm^2; (b): $\phi = 0.16$ j/cm^2

Fig. 4 Two frequency MPD spectrum of supersonically cooled CF_3Br seeded in Ar (90%). $\omega_1 = 1084.64$ cm^{-1}; $\phi_1 = 1.5$ J/cm^2; $\phi_2 = 3.5$ j/cm^2. Data are compared with the calculated spectrum reported on the bottom.

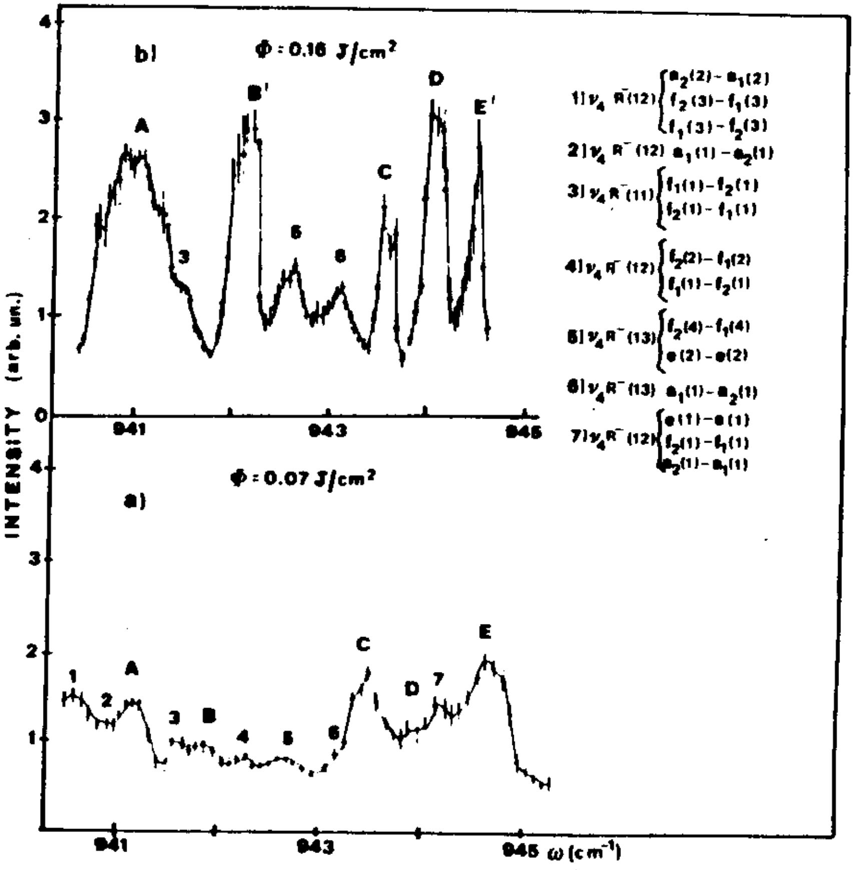




<n>
5
4
3
2
1
298°K
233°K
1080
1075
cm⁻¹
1070
1057
1056
ω(cm⁻¹)
ν_1
$2\nu_3$
$\nu_1 + 2\nu_3$
HOT BANDS



ABS ENERGY (mJ)
SLOPE 0.4 ± 0.05
SLOPE 0.8 ± 0.1
SLOPE 1.7 ± 0.1
SLOPE 0.8 ± 0.1
SLOPE 2.9 ± 0.1
10^{-1}
10^0
10^1
I (MW/cm²)



b)
Φ : 0.16 J/cm²
A
B'
C
D
E'
3
5
6
a)
Φ : 0.07 J/cm²
1
2
A
3
B
4
5
6
C
D
7
E
INTENSITY (arb. un.)
941
943
945
ω (cm⁻¹)
1) ν_4 $R^-(12)$ $a_2(2) - a_1(2)$, $f_2(3) - f_1(3)$, $f_1(3) - f_2(3)$
2) ν_4 $R^-(12)$ $a_1(1) - a_2(1)$
3) ν_4 $R^-(11)$ $f_1(1) - f_2(1)$, $f_2(1) - f_1(1)$
4) ν_4 $R^-(12)$ $f_2(2) - f_1(2)$, $f_1(1) - f_2(1)$
5) ν_4 $R^-(13)$ $f_2(4) - f_1(4)$, $e(2) - e(2)$
6) ν_4 $R^-(13)$ $a_1(1) - a_2(1)$
7) ν_4 $R^-(12)$ $e(1) - e(1)$, $f_2(1) - f_1(1)$, $a_2(1) - a_1(1)$

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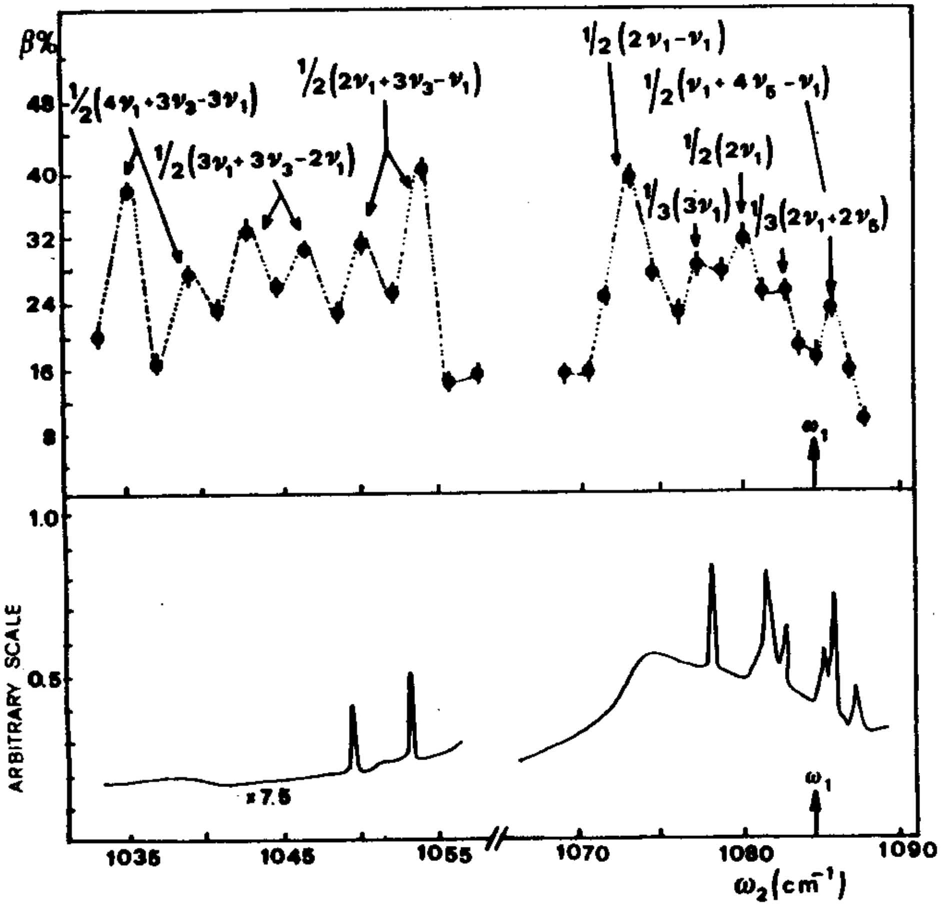
β%
48
40
32
24
16
8
½(4ν₁+3ν₃-3ν₁)
½(3ν₁+3ν₃-2ν₁)
½(2ν₁+3ν₃-ν₁)
½(2ν₁-ν₁)
½(ν₁+4ν₅-ν₁)
½(2ν₁)
⅓(3ν₁)
⅓(2ν₁+2ν₅)
ω₁
1.0
0.5
ARBITRARY SCALE
×7.5
ω₁
1035
1045
1055
1070
1080
1090
ω₂(cm⁻¹)