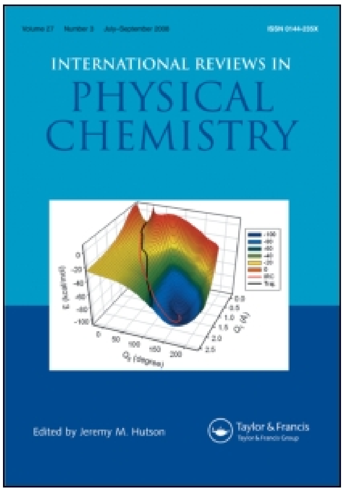

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Two-colour dip spectroscopy of jet-cooled molecules

Mitsuo Ito[a]
[a] Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan

To cite this Article Ito, Mitsuo(1989) 'Two-colour dip spectroscopy of jet-cooled molecules', International Reviews in Physical Chemistry, 8: 2, 147 — 169

To link to this Article: DOI: 10.1080/01442358909353227

URL: http://dx.doi.org/10.1080/01442358909353227

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1989, VOL. 8, NOS. 2/3, 147–169

Two-colour dip spectroscopy of jet-cooled molecules

By MITSUO ITO
Department of Chemistry, Faculty of Science,
Tohoku University, Sendai 980, Japan

In optical–optical double resonance spectroscopy, the resonance transition from an intermediate state to a final state can be detected by a dip of the signal (fluorescence or ion) associated with the intermediate state. This method probing the signal of the intermediate state may be called 'two-colour dip spectroscopy'. Various kinds of two-colour dip spectroscopy such as two-colour fluorescence/ion dip spectroscopy, two-colour ionization dip spectroscopy employing stimulated emission, population labelling spectroscopy and mass-selected ion dip spectroscopy with dissociation were briefly described, paying special attention to their characteristics in excitation, detection and application. They were extensively and successfully applied to jet-cooled large molecules and provided us with new useful information on the energy and dynamics of excited molecules.

1. Introduction

In optical–optical double resonance spectroscopy, a molecule in the ground state is excited to an intermediate excited state by one-photon absorption of ultraviolet/visible laser light (ν_1) and then the optical transition from the intermediate state to a final state is induced by the second ultraviolet/visible laser light (ν_2). When the optical transition with ν_2 is one-photon absorption, one can study a high excited state lying at $\nu_1+\nu_2$. We can also study a low-lying excited state by using stimulated emission from the intermediate state with ν_2. In this case, the final state detected is of energy $\nu_1-\nu_2$ ($\nu_1>\nu_2$). ν_1 can also be changed by changing the intermediate state. Therefore, the energy region covered by the double resonance spectroscopy is very wide: by the use of two ultraviolet/visible laser beams the state in a wide energy region from infrared to far-/vacuum-ultraviolet can be investigated. Another advantage of this spectroscopy is that the observed spectrum becomes very simple because only the transitions from a particular intermediate state occur. This is very useful, especially for the study of a high-energy region of a molecule where a number of rovibronic levels belonging to many different electronic states are heavily congested. The congestion can be resolved into many simple spectra obtained by selecting different intermediate states. The double resonance spectroscopy also provides a powerful means for the study of dynamical behaviour of an excited-state molecule. By taking a suitable time delay between the ν_1 and ν_2 pulses, one can follow the decay process of the intermediate state. Owing to these advantages, double-resonance spectroscopy is becoming popular in physics and chemistry.

In applying double-resonance spectroscopy to low-pressure gaseous molecules, there are two experimental ways of detecting the double-resonance transitions. One is to observe the signal associated with the final state. A typical spectroscopy of this kind is two-colour resonant enhanced multiphoton ionization (REMPI) spectroscopy, in which ions produced from the final state by auto-ionization or by photo-ionization are probed. Another way is to probe the signal associated with the intermediate state. The signal might be fluorescence from the intermediate state or ion signal directly associated with the intermediate state. Such a signal decreases by the successive ν_2 transition and exhibits a dip in the signal. This method of probing the signal of the intermediate state may be called two-colour dip spectroscopy. In the present paper, we are concerned with this spectroscopy, and various kinds of dip spectroscopy and their applications to rather large molecules and complexes will be described.

The most important criterion in double-resonance spectroscopy is the preparation of the excited molecules in a particular intermediate state. The preparation is usually achieved by one-photon (sometimes two-photon) absorption of ν_1 appropriate for the transition from the ground-state, but for room-temperature gases, the ground-state molecules are distributed over many low-lying vibrational levels, which are extremely congested in a large molecule. The transitions from these distributed ground-state levels also produce the intermediate state molecules distributed over many vibronic levels, even when we use monochromatic ν_1. Therefore, to ensure excitation to a particular intermediate state, the ground-state distribution should be suppressed by decreasing the temperature of the gas. The supersonic jet expansion of sample gas seeded in high-pressure rare gases produces ultra-cold molecules in the gas phase, which distribute almost entirely only to the lowest vibrational and rotational level in the ground state. Therefore the excitation of jet-cooled molecules with monochromatic ν_1 ensures the preparation of the molecules in a particular intermediate state. Full use of the advantages of double-resonance spectroscopy will be realized by applying the technique to jet-cooled molecules (Ito 1986, Ito *et al.* 1988). The importance of jet cooling becomes increasingly greater as the molecule becomes larger. Most of the molecules studied here are benzene derivatives, which are rather large molecules. Therefore two-colour dip spectroscopy is applied here exclusively to jet-cooled molecules.

The types of two-colour dip spectroscopy which will be discussed here are (1) two-colour fluorescence dip and ion dip spectroscopies, which are useful for the study of highly excited states of a molecule; (2) two-colour ionization dip spectroscopy using stimulated emission, which is a powerful tool for investigating the energetics and dynamics of the vibrational states of molecules in their electronic ground state; (3) population labelling spectroscopy, which is useful for the detection of the electronic state having a fast non-radiative decay; and (4) mass-selected ion dip spectroscopy involving dissociation, which is a new means for the study of the electronic excited states of a molecular ion. Each spectroscopy will be discussed with examples of its application obtained mainly in our laboratory.

2. Two-colour fluorescence dip spectroscopy—High excited states

Figure 1 shows the principle of this spectroscopy. Molecules in a jet are excited by the first laser light of ν_1 to a particular fluorescent A level and then the second laser light of ν_2 is introduced to excite the A state molecules to a higher excited state. In the presence of ν_1 the molecules in the A state emit fluorescence of a constant intensity. When the frequency ν_2 is resonant to a higher excited state R, the fluorescence intensity decreases because of the depopulation of the A state molecules caused by the R←A absorption. Therefore, by monitoring the total fluorescence while scanning ν_2, we obtain the fluorescence dip spectrum which corresponds to the R←A absorption.

Another way of monitoring the signal associated with the intermediate state is shown in figure 2. This is a method of monitoring the ion generated by one-photon resonant two-photon ionization in which the intermediate state A serves as a resonant

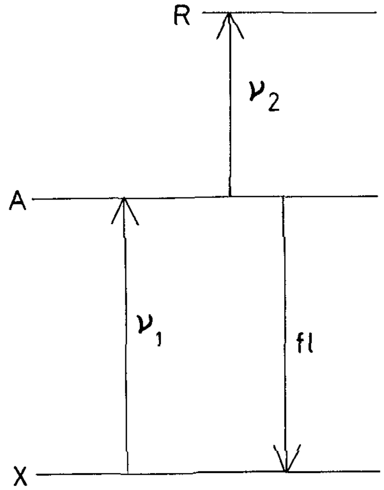

Figure 1. Principle of two-colour fluorescence dip spectroscopy.The fluorescence from the A state exhibits a dip when ν_2 is resonant to R.

state. In the presence of ν_1 alone, we have a constant ion current. When the R←A absorption occurs by ν_2, the ion current decreases because of the depopulation of the A state molecules. Therefore, in this case, the R←A transition can be observed in a form of ion-dip.

Although the principle of two-colour fluorescence/ion dip spectroscopy is very simple, its history is rather new. Two-colour fluorescence dip spectroscopy had been applied for the first time by Ebata *et al.* for the study of high excited states of NO (Ebata *et al.* 1982, 1983). Two-colour ion dip spectroscopy had also been used by Cooper *et al.* (1981, 1982) for I_2 and at almost the same time by Murakami *et al.* (1982) for toluene and aniline. Several applications of this spectroscopy for the study of high excited states (Ito and Fujii 1987) will be described here.

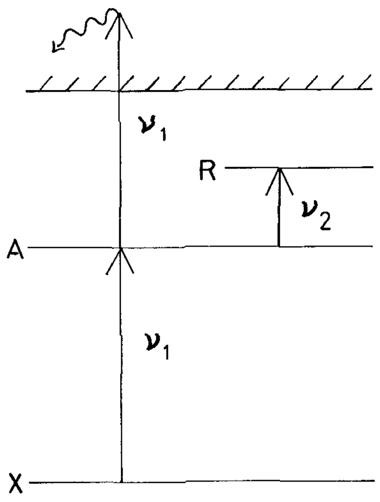

Figure 2. Principle of two-colour ion dip spectroscopy. The ion signal generated by one-colour (ν_1) one-photon resonant two-photon ionization exhibits a dip when ν_2 is resonant to R.

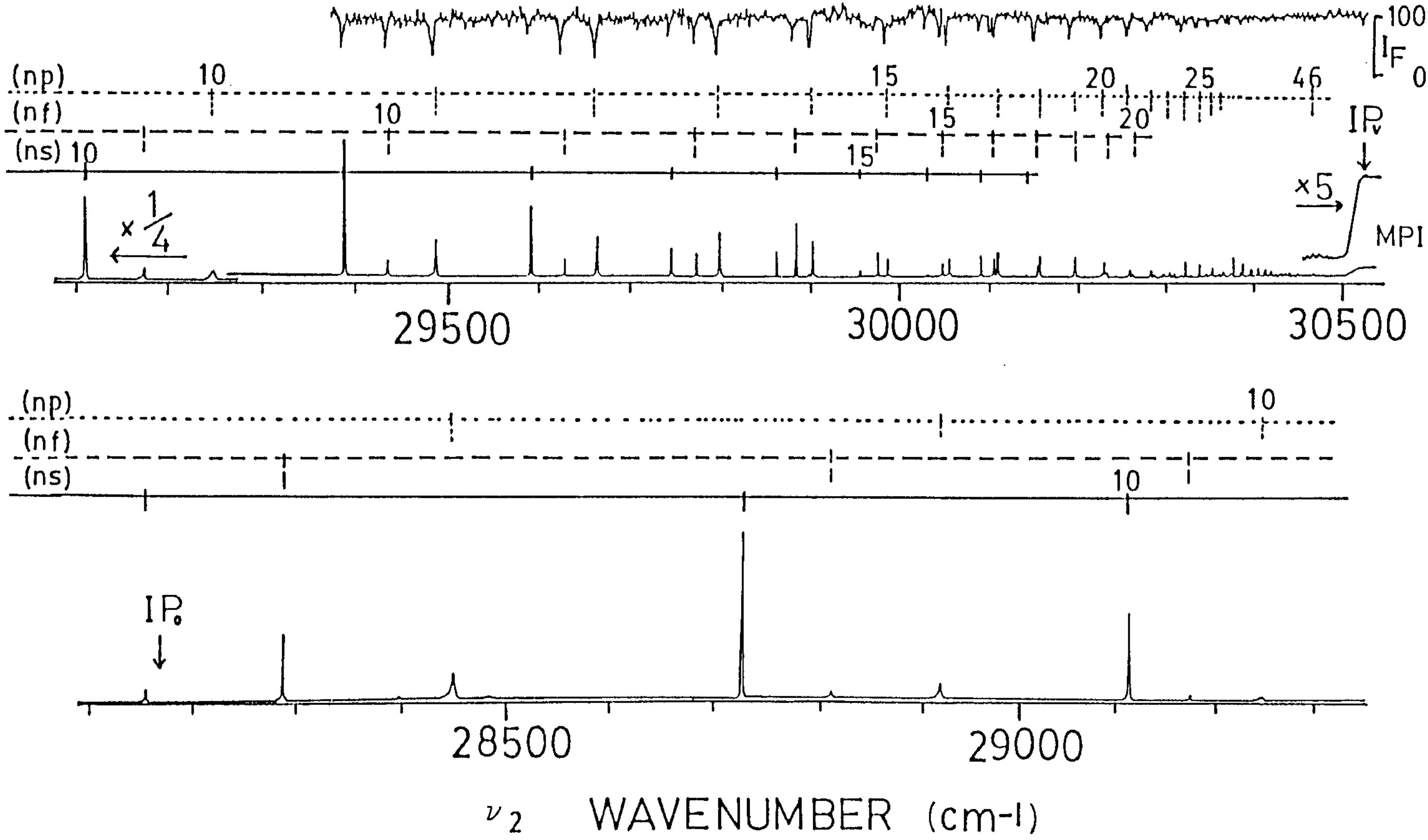

Figure 3. Two-colour multiphoton ionization (lower trace) and simultaneously measured fluorescence dip (upper trace) spectra of jet-cooled NO. The spectra were obtained by exciting the molecule to the $J=\frac{1}{2}$ $(N=0)$, $v=1$ level of the $A^2\Sigma^+$ state (at 46 541·05 cm^{-1}) with ν_1. The fluorescence dip spectrum in the region below $\nu_2=29\,400$ cm^{-1} is not shown.

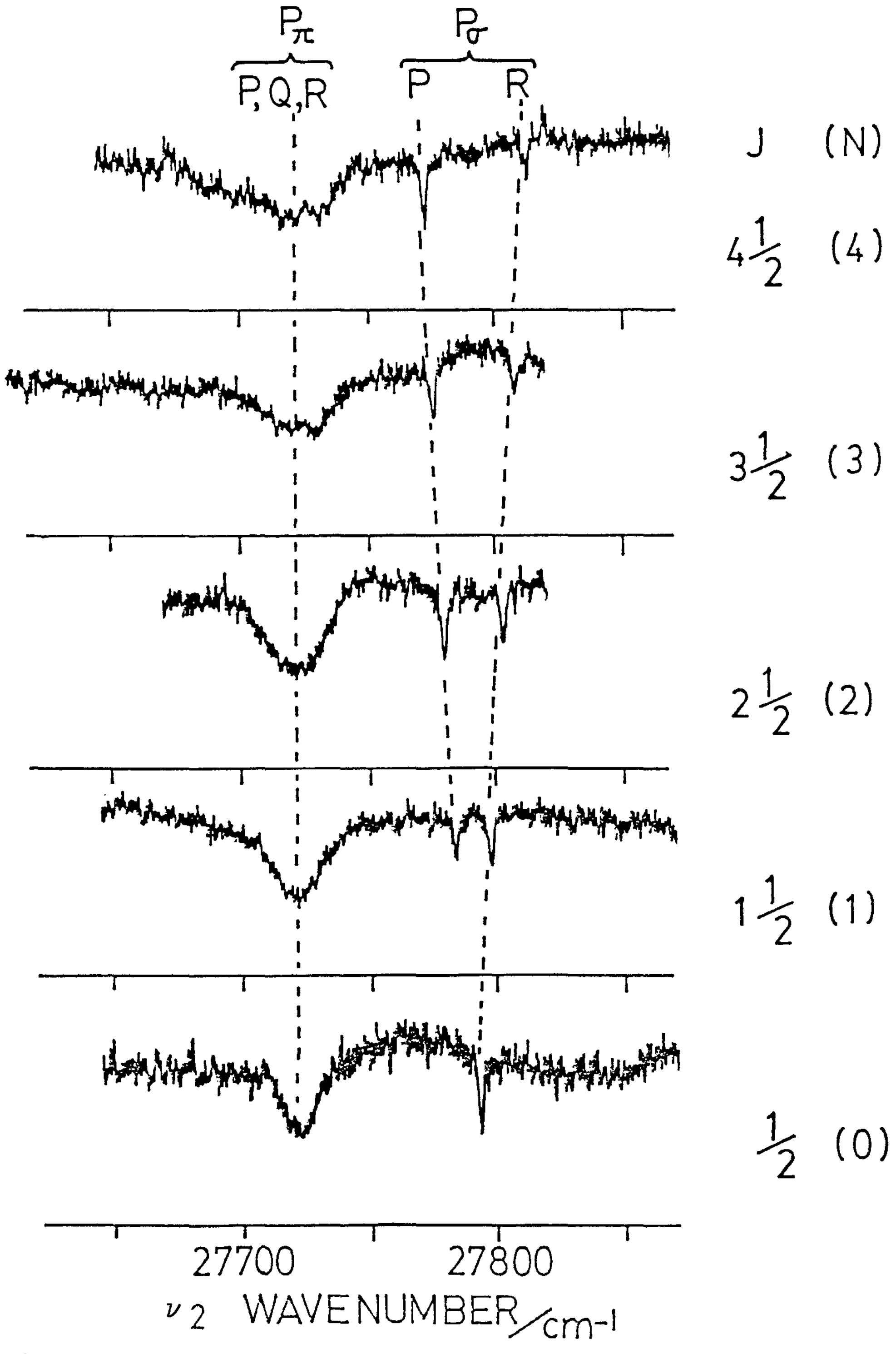

Figure 4. Two-colour fluorescence dip spectra of jet-cooled NO due to the transitions from various rotational levels in $A^2\Sigma^+$, $v=0$ to the 7p Rydberg state.

Figure 3 shows the optical–optical double resonance spectra of jet-cooled NO (Anezaki *et al.* 1985). Two spectra in the figure were both obtained by the selective excitation of the jet-cooled ground state molecule to the $J=\frac{1}{2}$ $(N=0)$, $v=1$ level of the $A^2\Sigma^+(3s\sigma)$ state (at $46\,541{\cdot}05\,\mathrm{cm}^{-1}$) with two-photons of ν_1 followed by further excitation of the excited molecules with ν_2 to higher excited states. The lower trace of the figure is the multiphoton ionization (MPI) spectrum obtained by probing the ions generated by the auto-ionization of the final high excited-state molecules. The upper one is the fluorescence dip spectrum obtained by monitoring the fluorescence from the intermediate A state. In both spectra, there appear three Rydberg series (*n*s, *n*f, *n*p, $n=8$–46) converging to the vertical ionization limit corresponding to the $v=1$ state of NO^+. Although there exists a good correspondence in the band position between the two spectra, the intensity relation of the three Rydberg series is quite different between them. The difference comes from the facts that the MPI intensity is determined by both the $R \leftarrow A$ transition probability and the auto-ionization yield of the R state, while the fluorescence dip intensity is determined only by the former. Therefore the fluorescence dip intensity faithfully reflects the $R \leftarrow A$ transition probability, which can be accurately determined from the measurements of the dip intensity against the ν_2 laser power. The transition probabilities of the individual bands in the three Rydberg series were determined from the observed dip intensities. It was found from the results that the $R \leftarrow A$ transition probability is proportional to n^{-3} (Anezaki *et al.* 1985). This proved for the first time the n^{-3} dependence of the Rydberg–Rydberg transition which had been predicted theoretically by Hartree (1928).

A great advantage of double-resonance spectroscopy is that we can obtain many simple spectra by selecting various intermediate states. From these simple spectra, the detailed energy levels of high excited state and their assignments are determined. Figure 4 shows as an example the two-colour fluorescence dip spectra of NO obtained by selecting different rotational levels ($J=\frac{1}{2}$–$4\frac{1}{2}$) in the $v=1$ level of the $A^2\Sigma^+$ state as an intermediate state (Anezaki *et al.* 1985). The spectra are due to the transitions from these selected rotational levels to the 7p Rydberg state. From these spectra, we can obtain the detailed rotational level structure of this Rydberg state. It is noted in the figure that the two sharp dips (P and R) in the high-frequency region are more separated as J increases. This fact clearly indicates that the 7p Rydberg state belongs to Hund case *b*. Since it is known that the Rydberg state with $n>8$ belongs to Hund case *d*, the transition from case *b* to *d* occurs at $n=7$–8 in NO. Such a transition had been theoretically predicted a long time ago, but its experimental confirmation was established for the first time by these results.

An application of the fluorescence dip spectroscopy to the study of high excited-states of a large polyatomic molecule is shown in figure 5. The upper trace of the figure shows the two colour fluorescence dip spectrum of jet-cooled DABCO (caged amine, see figure 5), obtained by selecting the $S_1 20^1$ level as an intermediate state and by monitoring the fluorescence from this intermediate state (Fujii *et al.* 1984). Many regular dips represent the transitions from the $S_1 20^1$ level to three kinds of Rydberg states ($\delta=0{\cdot}41$, $0{\cdot}23$ and $0{\cdot}11$, $n=10$–30) converging to the 20^1 vibrational level of the DABCO ion (at $59\,046\,\mathrm{cm}^{-1}$). It is proved from the figure that the two-colour fluorescence dip spectroscopy is a powerful tool for clear resolution of congested highly excited states of a large molecule such as DABCO. A similar spectrum can be also obtained by two-colour resonance-enhanced MPI spectroscopy. The lower trace of figure 5 shows the MPI spectrum due to the transitions from the same $S_1 20^1$ level to the high Rydberg states of jet-cooled DABCO in which the ion signal generated by the

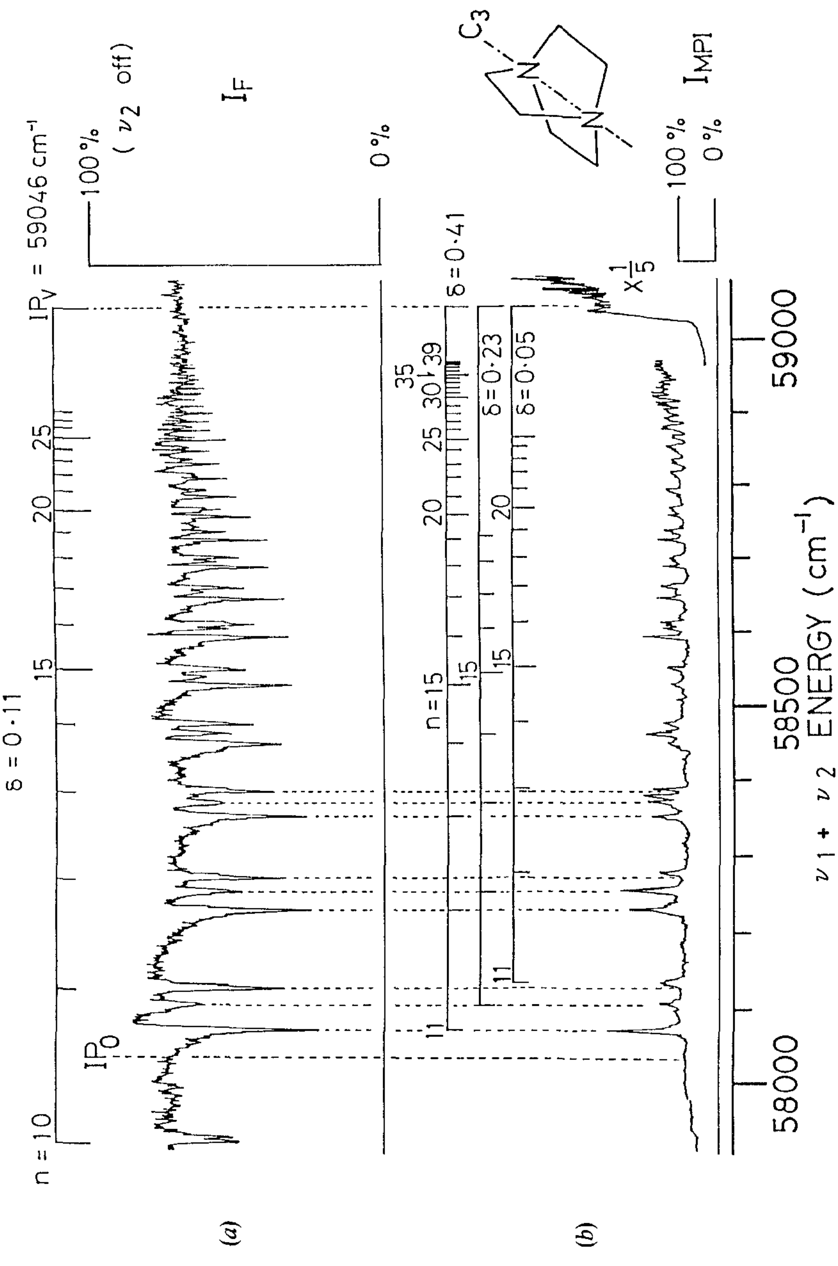

Figure 5. Two-colour fluorescence dip (*a*) and MPI (*b*) spectra of jet-cooled DABCO due to the transition from the $S_1 20^1$ (e', 1007 cm^{-1}) vibronic level for the energy region 58 000 ~ 59 000 cm^{-1}. The zero signal level (0%) and the signal level without ν_2 (100%) are indicated on the right-hand side of each spectrum. The adiabatic ionization potential IP_0 and the vertical ionization potential IP_v are also shown. Calculated Rydberg series are shown by solid lines.

auto-ionization of the Rydberg state is monitored (Fujii *et al.* 1983, 1984). It is seen from the figure that the MPI spectrum looks identical to the fluorescence dip spectrum, but there are several important differences between the two spectra. In the MPI spectrum, only the Rydberg states lying above the adiabatic ionization potential IP_0 appear because of the requirement for auto-ionization. On the other hand, there is no such restriction for the fluorescence dip spectrum, where the Rydberg states appear irrespective of the value of IP_0. In practice, many Rydberg states of $n=4$–10 lying below IP_0 were observed in the fluorescence dip spectrum (Fujii *et al.* 1984), as shown partly by the upper trace of figure 6. Therefore two-colour fluorescence dip spectroscopy has a great advantage for detecting high excited states over a wide energy region. In the case of DABCO, the energy region covered amounts to as wide as $10\,000\,\mathrm{cm}^{-1}$. Another marked difference is found between the MPI and fluorescence dip spectra in figure 5. A careful inspection of the two spectra shows that the two Rydberg series of $\delta=0{\cdot}41$ and $0{\cdot}23$ are common for both spectra, but the remaining one series differs between the two spectra. The latter series appearing in the fluorescence dip spectrum is one of $\delta=0{\cdot}11$, while the series in the MPI spectrum is of $\delta=0{\cdot}05$. The former series never appear in the MPI spectrum and the latter series never in the fluorescence dip spectrum. The result clearly indicates that the Rydberg state of $\delta=0{\cdot}11$ has a large transition probability in the transition from $S_1 20^1$, but it has a very small auto-ionization rate. The reverse is true for the Rydberg state of $\delta=0{\cdot}05$. This is a very clear example showing different dynamical behaviours of different Rydberg states.

As described in the beginning of this section, the same spectrum as that of fluorescence dip spectrum is obtained by two-colour ion dip spectroscopy. The lower trace of figure 6 shows the two-colour ion dip spectrum due to the same transitions of DABCO as before in which the ion signal generated by the one-colour (ν_1) one-photon resonant two-photon ionization with $S_1 20^1$ as a resonant state is monitored. It is seen that the ion dip spectrum is essentially the same as the fluorescence dip spectrum shown by the upper trace of figure 6. This is natural because both spectra reflect the decrease in population of the intermediate state caused by the ν_2 transition.

In both cases of NO and DABCO, the intermediate state chosen was a low-lying Rydberg state. Because of this selection, the high excited Rydberg states were selectively observed in the dip spectra of these molecules, because Rydberg–Rydberg transition has a large transition probability. In general, electronic transition between similar electronic states has a large transition probability. Therefore, in double resonance spectroscopy, high excited states similar in electronic structure to the selected intermediate electronic state are favourably detected. This characteristic may be used for the observation of a desired high excited state by selection of the kind of intermediate state. Consider, for example, a molecule such as conjugated ketone, aldehyde or nitrogen heterocyclic, which has two kinds of electronic excited state, that is, n,π^* and π,π^*. In usual one-photon absorption from S_0, $S_n(\pi,\pi^*)$ states appear strongly in the spectrum, while $S_n(n,\pi^*)$ states except $S_1(n,\pi^*)$ are hardly observed because the weak $S_n(n,\pi^*)\leftarrow S_0$ transition is obscured by the strong $S_n(\pi,\pi^*)\leftarrow S_0$ transition. Therefore, our information on the high excited $S_n(n,\pi^*)$ states is very limited. However, since $S_n(n,\pi^*)$ is similar in its electronic structure to $S_1(n,\pi^*)$, the $S_n(n,\pi^*)\leftarrow S_1(n,\pi^*)$ transition will have a large transition moment. Therefore, when we use the $S_1(n,\pi^*)$ state as an intermediate resonance state in double-resonance spectroscopy, the high excited $S_n(n,\pi^*)$ states will be selectively observed. (The $S_n(\pi,\pi^*)$ states do not appear strongly because of a small $S_n(\pi,\pi^*)\leftarrow S_1(n,\pi^*)$ transition moment).

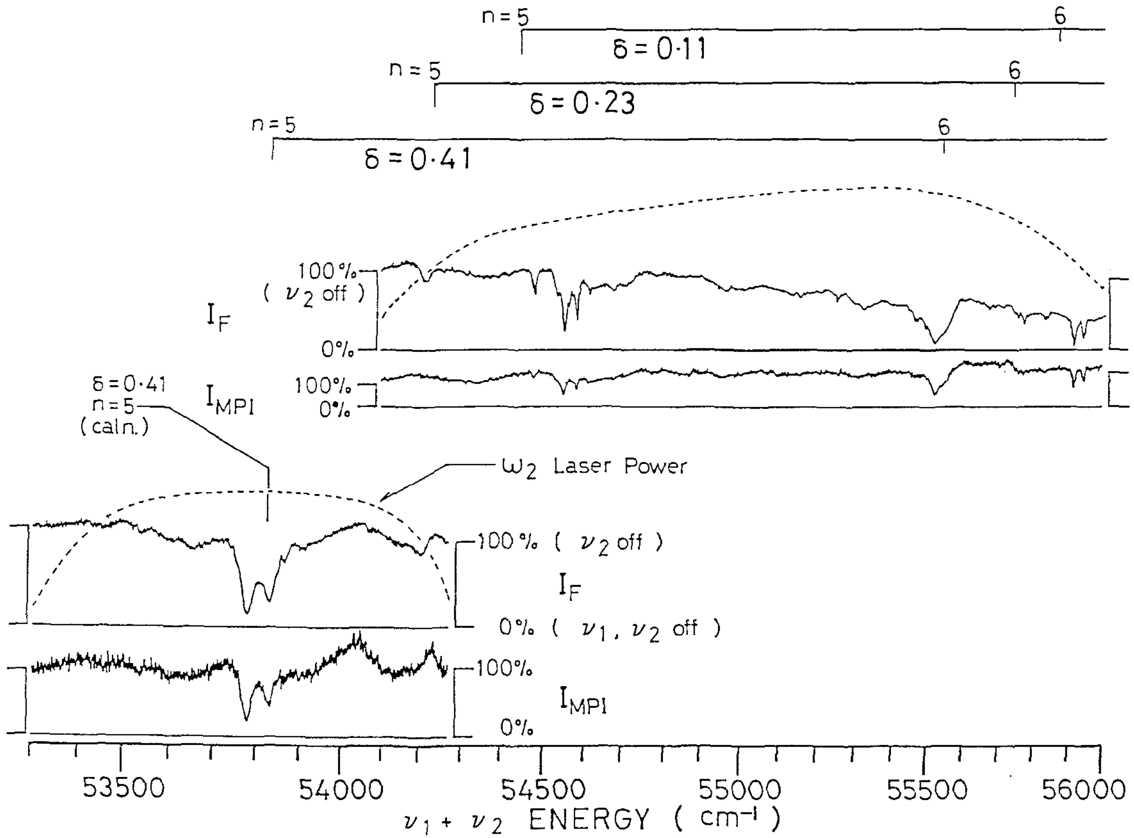

Figure 6. Two-colour ionization dip (lower trace) and fluorescence dip (upper trace) spectra of jet-cooled DABCO due to the transition from the $S_1 20^1$ level. The spectra (53 300–56 000 cm^{-1}) are divided into two lasing regions of ν_2 laser dye (C-540A and R-6G). Relative laser power of ν_2 is shown by broken curve. The zero signal level (0%) and the signal level without ν_2 (100%) are indicated on both sides of each divided spectrum. Calculated Rydberg series are indicated by solid lines.

With the expectation, Goto *et al.* (1985) have measured the two-colour fluorescence dip spectrum of jet-cooled glyoxal by using the $S_1(n, \pi^*)$ state as an intermediate state. They could observe for the first time the $S_n(n, \pi^*)$ state of isolated glyoxal by this method. Glyoxal has the $T_1(n, \pi^*)$ state at 2500 cm^{-1} lower than the $S_1(n, \pi^*)$ state. This $T_1(n, \pi^*)$ state is phosphorescent. Therefore, if we use this $T_1(n, \pi^*)$ state as an intermediate state and observe the phosphorescence dip spectrum, we should selectively detect $T_n(n, \pi^*)$. The $T_n(n, \pi^*)$ state of glyoxal was actually observed by this method (Goto *et al.* 1985). It was concluded from these studies that the energy separation between the corresponding $S_n(n, \pi^*)$ and $T_n(n, \pi^*)$ states is almost constant irrespective of n and it is 2500–2800 cm^{-1}. Similar two-colour fluorescence dip and phosphorescence dip spectra were measured also for jet-cooled pyrazine and the location of high excited $S_n(n, \pi^*)$ and $T_n(n, \pi^*)$ states was determined (Goto *et al.* 1987a).

Besides those molecules mentioned above, the highly excited states of ABCO (Fujii *et al.* 1985), benzene (Kakinuma *et al.* 1987), pyrazine (Goto *et al.* 1987b) and *p*-difluorobenzene (Fujii *et al.* 1986) have been investigated by two-colour fluorescence/ion dip spectroscopy.

3. Two-colour ionization dip spectroscopy using stimulated emission—Ground state vibrational levels

Optical–optical double-resonance spectroscopy is powerful not only for the study of high excited-states of a molecule but also for the ground-state molecules. The first laser light of ν_1 promotes jet cooled S_0 molecules to a particular (ro)vibronic level (intermediate state) in S_1, and the excited S_1 molecules are subject to stimulated emission by the second laser light of ν_2, the molecules being transferred to the final vibrational level of the ground-state molecule (see figure 7). Information obtained by the stimulated emission from the excited electronic state to the ground-state vibrational levels is the same as that of infrared and Raman spectroscopy. However, the stimulated emission spectroscopy has the following advantages over infrared and Raman spectroscopy.

1. There is no severe vibrational selection rule except the Franck–Condon factor for the transition between vibrational levels in S_1 and S_0. Therefore transitions involving multiple vibrational quantum change are possible, in contrast to the requirement of $\Delta v = \pm 1$ for Raman and infrared transitions. As a result, high vibrational levels are easily detected.
2. The spectral resolution is determined simply by the ν_2 laser resolution. Therefore the stimulated emission spectroscopy is a high-resolution spectroscopy and has a great advantage, especially for the study of the high-vibrational-energy region, where the levels are heavily congested.
3. By measuring the ν_2 laser power dependence on the stimulated emission, information about the dynamics of the ground-state vibrational levels can be obtained.

There are several ways for the observation of the stimulated emission from S_1. When S_1 is fluorescent, the stimulated emission can be observed in a form of fluorescence dip (figure 7(*a*)). This method has been developed by the MIT group (Kittrell *et al.* 1981, Vaccaro *et al.* 1983) and called stimulated emission pumping (SEP). The second method is to monitor the ion signal generated by S_1 resonant multiphoton ionization and the stimulated emission from S_1 is detected as a dip of the ion signal (see figure 7(*b*)).

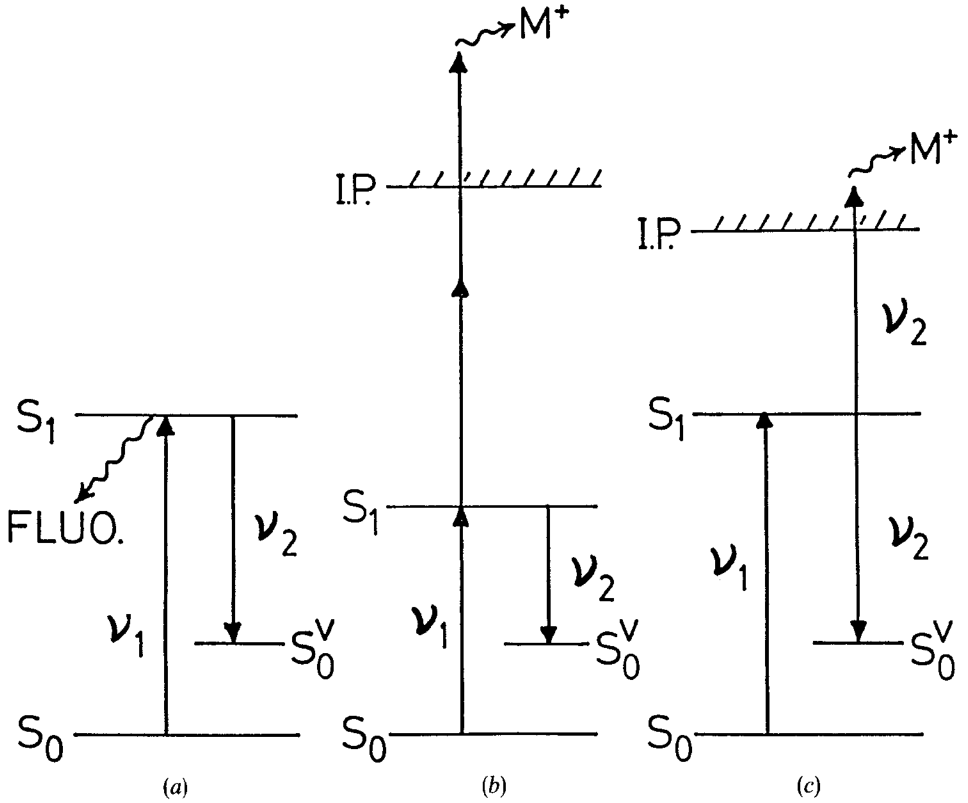

Figure 7. Three detection methods of ν_2 stimulated emission from the ν_1-pumped S_1 level to the ground-state vibrational level S_0^v. (*a*) the dip of fluorescence from S_1 is monitored (stimulated emission pumping), (*b*) the dip of one-colour (ν_1) REMPI signal is monitored and (*c*) the dip of the ion current produced by $\nu_1+\nu_2$ ionization is monitored (two-colour ionization dip spectroscopy using stimulated emission). In (*c*), ν_2 plays dual roles of ionization and stimulated emission.

This method has been used for the first time by Cooper *et al.* (1981, 1982) and almost simultaneously by Murakami *et al.* (1982). The third method is one recently proposed by Suzuki *et al.* (1986) and called two-colour ionization dip spectroscopy employing stimulated emission. We shall explain this spectroscopy in detail.

The principle of the method is shown in figure 7 (*c*). A molecule in S_0 is excited to a particular level in S_1 with ν_1 and the S_1 molecule is further excited to the ionization continuum with ν_2. We monitor the ion signal generated from the continuum. The laser power of ν_1 is suppressed as low as possible, so that multiphoton ionization with ν_1 alone is avoided. Therefore the ion signal occurs only when ν_1 and ν_2 coexist. The laser light of ν_2 is also used for the stimulated emission from S_1. When ν_2 is resonant to a vibrational level in S_0, the stimulated emission occurs and the S_1 population decreases. The decrease of the S_1 population is reflected by the dip of the ion signal. In this method, ν_2 had dual roles of the ionization and stimulated emission. This is an advantage of this method and also simultaneously a disadvantage as described below.

In any double-resonance experiment, spatial matching of the two laser beams is a most difficult problem. Consider the case of stimulated emission pumping. All the sample molecules irradiated by the ν_1 beam contribute to the fluorescence signal, while the stimulated emission occurs only for the sample portion where ν_1 and ν_2 overlap. Therefore, when we have spatial mismatching of the two laser beams, the fluorescence dip intensity becomes small compared with the case of complete matching. Since the complete matching of two different laser beams is practically impossible, the dip intensity usually becomes very small. On the other hand, in the case of ionization dip spectroscopy, both ionization and stimulated emission occur only for the sample portion where ν_1 and ν_2 overlap. As a result, the ion dip intensity measured as a percentage is not seriously influenced by mismatching of the laser beams, and we can obtain a quantitative dip intensity, which is essentially important in discussion of the dynamics of ground-state vibrational states, as will be shown later. The fact that the ion dip intensity is not seriously influenced by the laser mismatching is also an important factor for the measurement over a wide frequency region of ν_2.

A disadvantage of the two-colour ionization dip spectroscopy is that the vibrational energy region in S_0 studied is restricted by

$$0 < E_{\mathrm{vib}} < 2h\nu_1 - IP_0,$$

where IP_0 is the adiabatic ionization potential of a molecule. The energy region beyond the upper limit will be studied by the stimulated emission pumping method.

Figure 8 shows as an example the two-colour ionization dip spectrum of jet-cooled aniline due to stimulated emission from the zero-point level of S_1 to the ground-state vibrational levels in the frequency region from 800 to 3200 cm^{-1} (Suzuki *et al.* 1988). For comparison, the ordinary fluorescence spectrum from the same zero-point level in S_1 is also shown. It is seen that a large number of sharp dips appear in the entire spectral region in the ionization dip spectrum. The spectrum looks noisy, but even a very weak dip is reproducible and actually represents the ground-state vibrational level. It is evident by comparison of the two spectra in the figure that the numbers of the vibrational levels detected by the ionization dip method are much larger than those obtained from the fluorescence spectrum. It is also noted that the spectral resolution is much better in the ionization dip than the fluorescence spectrum. The resolution of the former is determined by the laser resolution, but that of the latter by the resolution of a monochromator used.

The example of jet-cooled aniline clearly shows that the two-colour ionization dip spectroscopy employing stimulated emission is a high-resolution and high-sensitivity spectroscopy which is very useful for the study of ground-state vibrational levels. Therefore the application of this spectroscopy may be extended to a species of very low concentration, such as a van der Waals molecule or a hydrogen-bonded complex. Such an example is shown in figure 9, in which the two-colour ionization dip spectra employing stimulated emission of jet-cooled phenol and a phenol–water (1 : 1) hydrogen-bonded complex are shown (T. Ebata, M. Furukawa, T. Suzuki and M. Ito, unpublished work). Both spectra represent the stimulated emission from the S_1 zero-point levels of the respective species. The two spectra were taken with nearly the same laser powers of ν_1 and ν_2, but the concentration of the complex in the jet is much smaller than that of bare phenol. As seen from the figure, the ionization dip is generally very weak for bare phenol, but the dip becomes greatly enlarged by the formation of the complex. The observed phenomenon may be qualitatively explained as follows. In the stimulated emission from S_1, the population of the S_1 state molecules decreases in proportion to the transition probability. However, the molecule in ground-state vibrational level reached by the ν_2 stimulated emission will come back again to the S_1

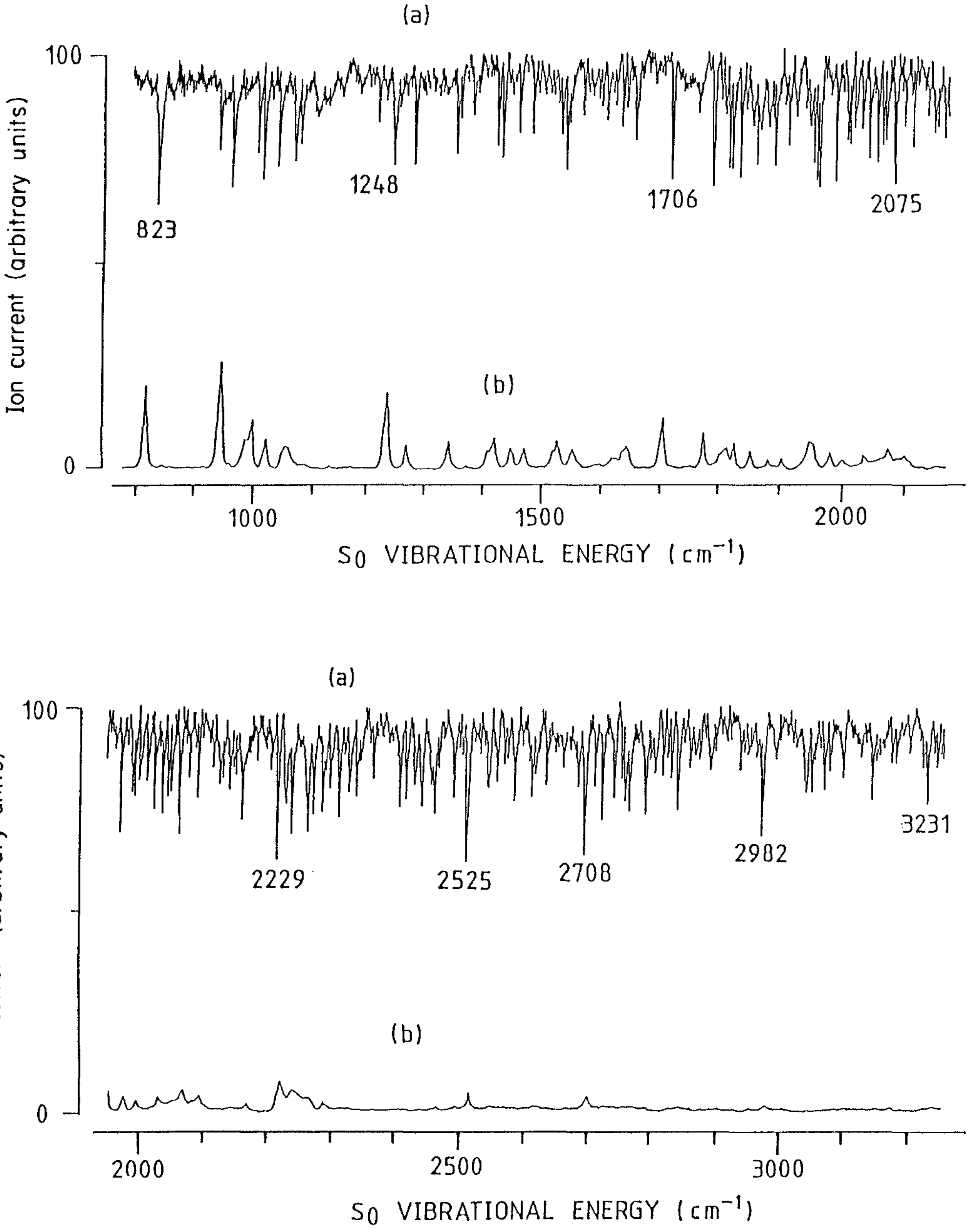

Figure 8. Two-colour ionization dip spectrum of jet-cooled aniline (*a*) and corresponding fluorescence spectrum (*b*). In both spectra, the molecule was pumped to the S_10^0 level.

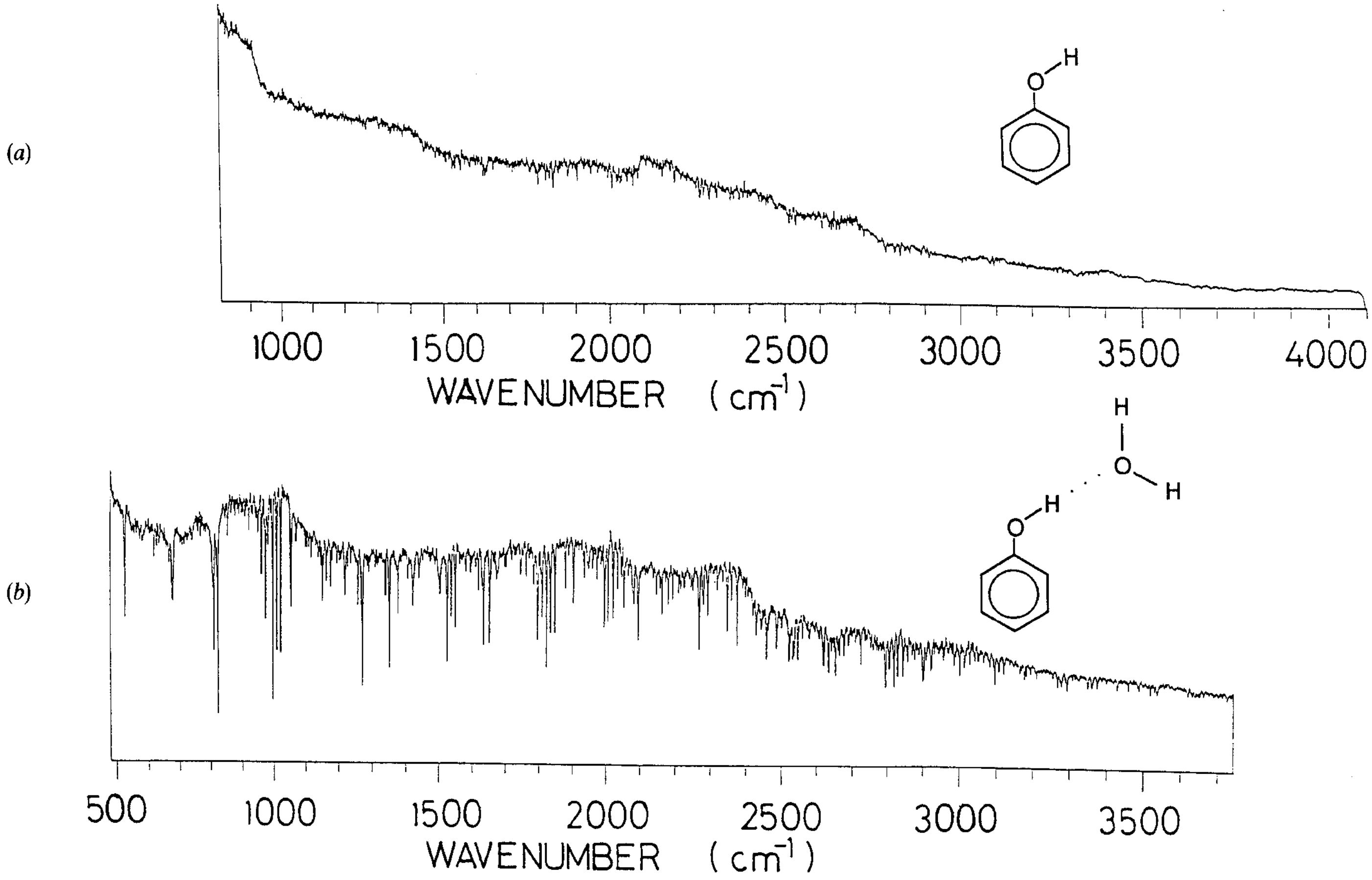

Figure 9. Two-colour ionization dip spectra of jet-cooled bare phenol (*a*) and phenol–water hydrogen bonded complex (*b*). Both spectra represent stimulated emission from $S_1 0^0$ of respective species.

state by the re-absorption of ν_2. The chance of the re-absorption is determined by the lifetime of the vibrational level, which is determined by the intramolecular vibrational redistribution (IVR) rate. Therefore, when the IVR rate is small, that is, when the lifetime is long, the molecules have a great chance to come back to the S_1 state; as a result, the dip intensity becomes small. On the other hand, the dip intensity becomes large when the IVR rate is large. In the case of the phenol–water hydrogen-bonded complex, many new low-frequency hydrogen-bond modes appear, arising from the complex formation, in addition to the intramolecular modes of phenol itself. As a result, the density of the vibrational states increases greatly. This leads to a great enhancement of the IVR rate by complex formation. Semi-qualitative analysis of the dip intensity shows that the IVR rate is enhanced by a factor of more than 10^2 by the complex formation. In general, the experimental means for the evaluation of the IVR rate of a ground-state vibrational level are very few. In this respect, ionization dip spectroscopy has a great opportunity to become a powerful tool for the study of the dynamics of the ground-state vibrational level. Moreover, the well resolved ionization dip spectrum of the phenol–water complex shown in figure 9 demonstrates the high potential of this spectroscopy for the study of detailed vibrational level structure in S_0 of a species of very low concentration. Such information is never to be expected from infrared and Raman spectroscopy.

4. Population labelling spectroscopy—Excited state having a fast non-radiative decay

Population labelling spectroscopy is one of the optical–optical double-resonance spectroscopy which is widely used for the assignment of the complex rovibronic structure of the electronic spectrum of a diatomic molecule (for example Kaminsky *et al.* (1976)). The principle of this spectroscopy is briefly explained in figure 10. The frequency of ν_2 is fixed to a well assigned absorption band, due to the transition from a

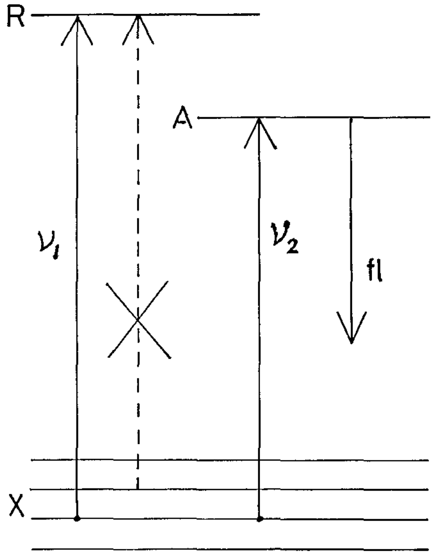

Figure 10. The principle of population-labelling spectroscopy. The fluorescence from the A state which is reached by ν_2 absorption from a particular level in X is monitored. The fluorescence intensity decreases when ν_1 is resonant with the transition from the particular level in X to the R state.

particular level X in the ground state to a particular excited electronic level A, and the fluorescence from the A state is probed. Another tunable laser light of ν_1 is introduced and this induces the transition to another electronic excited state R. When the frequency of ν_1 is scanned, causing the transition to the R state from the particular ground state level X common to the A←X transition, the intensity of the fluorescence from the A state decreases because of the depopulation of the X state molecules caused by the R←X absorption. Therefore, by monitoring the fluorescence caused by the A←X excitation, the R←X transition in which X is common to A←X is observed in a form of fluorescence dip and then the X level in R←X can be definitely identified. Since X is labelled by knowing the A←X transition, this spectroscopy is called population labelling and it is particularly useful for the assignment of a hot band in the electronic spectrum of a diatomic molecule.

This spectroscopy can also be applied to large polyatomic molecules. The application of this spectroscopy to jet-cooled azulene is briefly described here (Suzuki and Ito 1987). Figure 11 shows the electronic states of azulene. It is well known that the azulene molecule has an unusual emission property; S_1 is non-fluorescent, but S_2 highly fluorescent. The non-emissive character of S_1 is due to the existence of a very fast internal conversion in S_1. It is also known that the oscillator strength of the $S_1 \leftarrow S_0$ absorption is very small (0·009) and the measurement of the absorption for the room temperature vapour requires an absorption cell of as long as 4 m (Hunt and Ross 1962). We want to measure such a weak transition for jet-cooled molecules of extremely low concentration prepared by supersonic jet expansion. Since S_1 is non-fluorescent, the fluorescence excitation method is useless. If we use the S_1 resonant enhanced multiphoton ionization technique, at least five photons are required for the ionization. Therefore the MPI method is also difficult to apply.

However, it is possible to measure the $S_1 \leftarrow S_0$ transition of jet-cooled azulene by using the characteristic emission property of this molecule and by applying population labelling spectroscopy. The S_1 state has a very fast non-radiative decay process, so that the S_1 molecules prepared by the $S_1 \leftarrow S_0$ absorption are rapidly depopulated. The

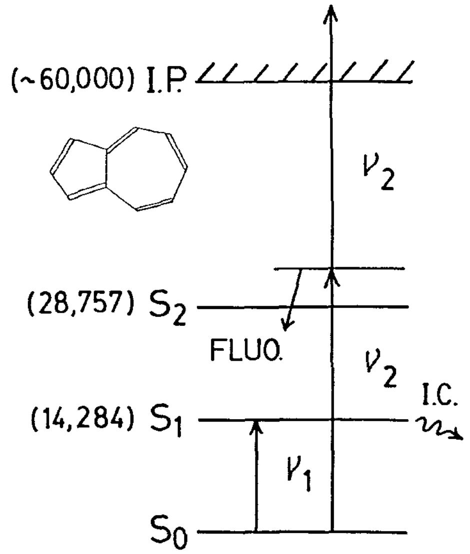

Figure 11. Schematic diagram of population-labelling spectroscopy of jet-cooled azulene.

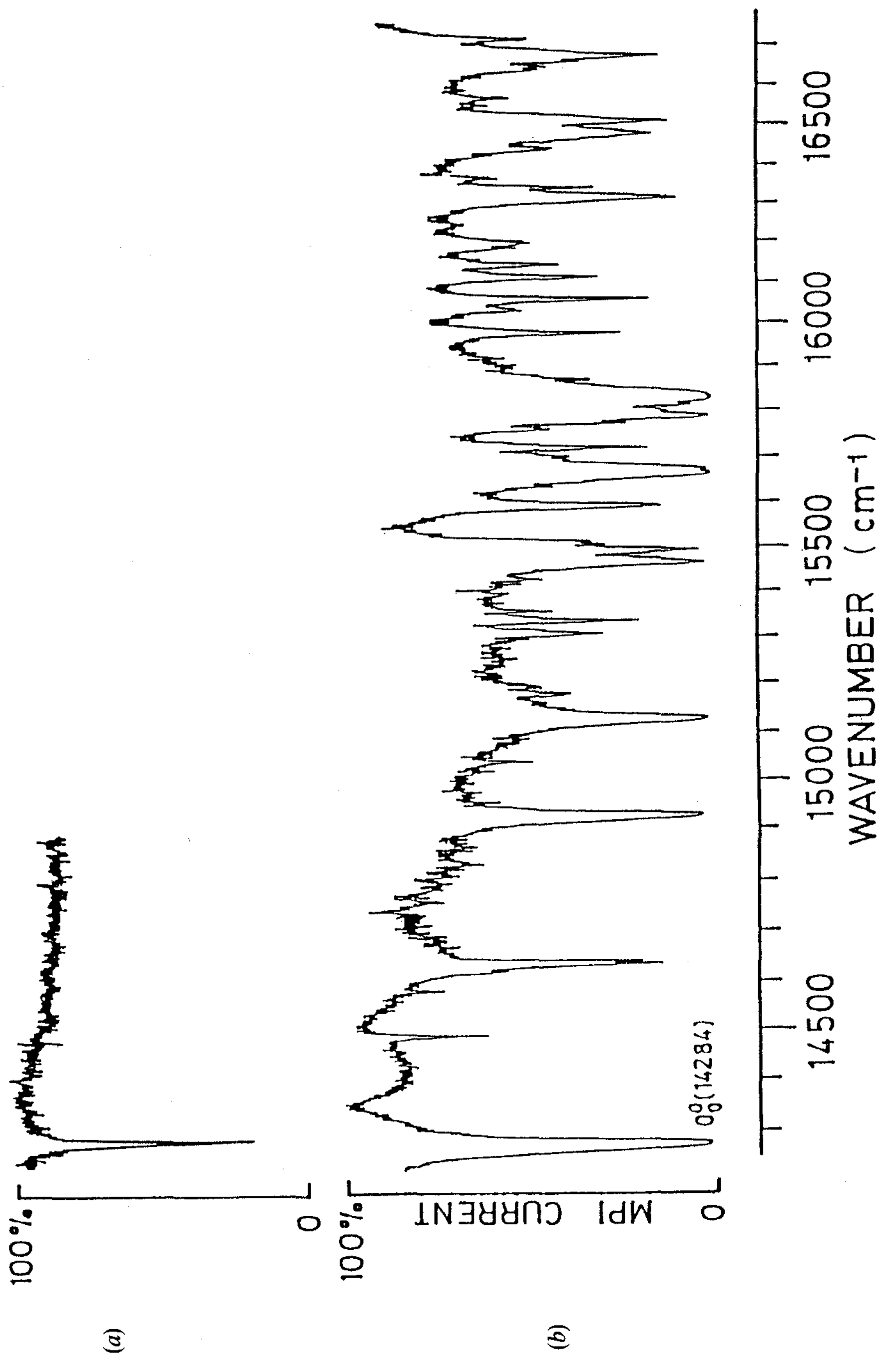

Figure 12. $S_1 \leftarrow S_0$ spectra of jet-cooled azulene obtained by population labelling spectroscopy with the ν_1 laser powers of 57 μJ per pulse (*a*) and 1 mJ per pulse (*b*).

depopulation causes efficient pumping up of the S_0 state molecules by ν_1, resulting in a great decrease of the S_0 population. This S_0 depopulation is probed by the signal associated with a particular level in S_2 which is excited by fixed ν_2 from the S_0 state. The signal associated with the particular S_2 level is either the fluorescence from the particular level or the ion signal generated by one-photon resonant enhanced two-photon ionization with the particular level as a resonant state (see figure 11). By probing such a signal while scanning the frequency of ν_1, the $S_1 \leftarrow S_0$ transition is observed as a dip of the signal.

Figure 12 shows the $S_1 \leftarrow S_0$ spectrum of jet-cooled azulene obtained by the above method. The spectrum in the figure is one measured by monitoring the ion signal generated by the resonant enhanced multiphoton ionization. The same spectrum was also obtained by probing the fluorescence from S_2. It is seen from the figure that a well resolved vibrational structure is developed from the 0, 0 band at $14284\,\mathrm{cm}^{-1}$ toward higher frequency side. Figure 12(*a*) is the spectrum obtained with weak power of ν_1 (57 μJ per pulse), where only the 0, 0 band appears. Figure 12(*b*) is one obtained with large power of ν_1 (1 mJ per pulse), where a number of bands appear beside the 0, 0 band. It is noted in figure 12(*b*) that the ion signal is almost zero for the strong bands including the 0, 0 band. This means that the population of the S_0 molecules becomes zero for these transitions. The complete depopulation clearly demonstrates the existence of a very fast relaxation process in S_1.

It is possible to estimate the non-radiative relaxation rate of S_1 from the observed width of each vibronic band. Careful measurements of the band width with high-resolution laser light and of the laser power dependence on the width show that the band width due to homogeneous broadening amounts to as much as $4\text{–}5{\cdot}5\,\mathrm{cm}^{-1}$. The internal conversion rate of S_1 evaluated from the width is $1 \times 10^{12}\,\mathrm{s}^{-1}$, which is about four orders of magnitude larger than the rate for S_2 ($2{\cdot}2 \times 10^{8}\,\mathrm{s}^{-1}$).

As was demonstrated by the case of azulene, the population labelling method is very useful for the detection of excited states which have very fast non-radiative relaxation processes. In general, high excited valence states of large polyatomic molecules have various fast non-radiative relaxation processes. Such high excited states may be studied under the supersonic jet condition by labelling the known $S_1 \leftarrow S_0$ transition.

5. Mass-selected ion dip spectroscopy using dissociation-excited states of cations

The spectroscopy of ions in the gas phase has many experimental difficulties. The first is a problem in preparation of gaseous ions. Gaseous ions are usually produced by electron impact on neutral molecules in the gas phase. Since fine control of the electron energy is very difficult and also particle collisions are used, the ions produced by electron impact have widely distributed internal energies. As a result, the electronic spectrum of the ions becomes broad by overlapping of transitions from the many distributed levels. Secondly, a highly sensitive spectroscopy is required for ion spectroscopy, since the concentration of ions is usually very small. However, the highly sensitive spectroscopic means like fluorescence excitation or multiphoton ionization that are often used for neutral molecules cannot be applied to ions; many polyatomic ions are non-fluorescent and the ionization potential is very high, especially for cationic species. From these reasons, the present status of ion spectroscopy is very poor compared with that of the spectroscopy of neutral molecules, and the establishment of a new ion spectroscopy based on a new principle is eagerly desired.

Cations in the gas phase can be easily generated by photo-ionization of neutral molecules. In particular, resonant enhanced multiphoton ionization is a very efficient means for the production of cations. When choosing a suitable resonance state in the ionization, it is possible to prepare the ground-state cations selectively distributed in a particular vibrational level. The next problem is how to measure the electronic spectrum of such a state-selected cation. As mentioned above, the fluorescence excitation method cannot be used because of the non-fluorescent property of large polyatomic cations. (Diatomic cations are usually fluorescent and the fluorescence excitation method can be applied to them.) The non-emissive property of a large polyatomic cation implies the existence of efficient non-radiative relaxation processes in its excited state. For a low-lying electronic excited state, internal conversion to the ground state will be an important non-radiative process. (Intersystem crossing is in general absent for the lowest excited doublet state because the quartet state is at higher energy.) In addition to the internal conversion, the dissociation of the excited state cation is also important. It is well known that the multiphoton ionization (MPI) of a neutral molecule with powerful laser light generates many fragmented species beside the parent cation (for example Neusser (1987)). The number of the fragmented species increases at the expense of the parent cations with increase of the laser power. This shows that the parent cation in the electronic ground state produced by MPI dissociates in an excited state which is reached by the absorption of one or more photons from the ground state. Since the dissociation is in general efficient, this characteristic may be used to measure the electronic spectrum of a cation. The spectroscopy using the above characteristic is mass-selected ion dip spectroscopy employing dissociation, and its principle is shown in figure 13.

Jet-cooled neutral molecules in S_00^0 are ionized by one-colour (ν_1) resonant enhanced two-photon ionization. When a suitable vibronic level in S_1 is selected as a resonance state, we can prepare the ground-state parent cations in a particular vibrational level. The parent cations thus produced are mass-selected by a quadrupole mass filter and detected. Then the second tunable laser light of ν_2 excites the ground-state parent cations to an electronically excited state where the excited parent cation dissociates directly or indirectly into smaller fragmented species. As a result of the dissociation, the signal of the mass-selected parent ion decreases and gives an ion dip. Therefore, when the mass-selected parent cations are detected while scanning the laser frequency of ν_2, we obtain an ion-dip which represents the transition from the state-selected ground state of the cation to an excited state from where the dissociation occurs. This spectroscopy has been developed for the first time by Syage and Wessel (1987) and subsequently by Tsuchiya *et al.* (1989). A similar spectroscopy employing the dissociation of cation was recently developed by Schlag's group (Kakoschke *et al.* 1985, Weinkauf *et al.* 1987, Walter *et al.* 1988, 1989) and by Ripoche *et al.* (1988). They detected the fragmented cation of a specific mass resulting from the dissociation of the parent cation, and they successfully observed the electronic transitions of the cations of COS, CH_3I, benzene and chlorobenzene.

Tsuchiya *et al.* (1989) applied the mass-selected ion dip spectroscopy to the jet-cooled cations of benzene, *p*-difluorobenzene and 1,3,5-trifluorobenzene and successfully obtained their electronic spectra. The usefulness of this spectroscopy is demonstrated here for the case of the *p*-difluorobenzene cation. This cation is non-fluorescent and its electronic spectrum in the gas phase has never been observed. Before showing its mass-selected ion dip spectrum, the preparation of the ground state cation (D_0) in a particular vibrational level will be briefly mentioned. The adiabatic ionization

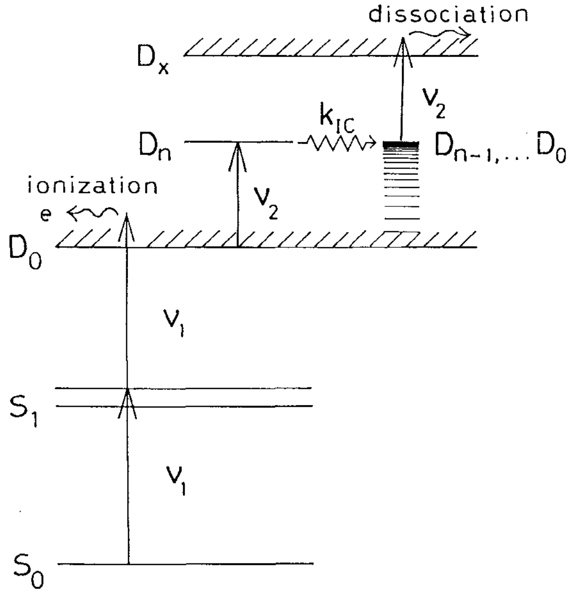

Figure 13. Schematic diagram showing the principle of mass-selected ion dip spectroscopy for detecting the $D_n \leftarrow D_0$ transition of the cation prepared by 1+1 REMPI of a neutral molecule. The figure shows the case in which the cation dissociates in the dissociative D_x state excited by the absorption of one more ν_2 photon from the lower energy doublet states $D_{n-1}, \ldots, D_0$ which are produced by the internal conversions of the D_n cation. There are of course a variety of dissociation mechanisms.

potential (IP_0) of *p*-difluorobenzene is 73 871 cm^{-1}. Since the origin of S_1 is at 36 840 cm^{-1}, the two-photon energy of this frequency is not enough for the ionization. The lowest frequency vibronic band in S_1 which can be used as a resonant state in the one-colour (ν_1) resonant enhanced two-photon ionization is $S_1 17b^2_0$ at 37 080 cm^{-1}. When we use this band in MPI, the excess energy possessed by the parent cation produced is 289 cm^{-1}. Therefore the cations should be distributed in vibrational levels less than 289 cm^{-1}. In order to determine the vibrational level distribution, the two-colour ionization threshold spectrum of jet-cooled *p*-difluorobenzene was observed by using $S_1 17b^2_0$ as a resonance state. Only one sharp ionization threshold was found at 238 cm^{-1} in the excess energy region less than 289 cm^{-1}, and no threshold was found at IP_0. Since 238 cm^{-1} is assigned to $17b^2$ of the cation, the above result clearly shows that the parent cations produced are exclusively in the $17b^2$ vibrational level in the ground state; the selective ionization of $\Delta v = 0$, that is, the transition from $S_1 17b^2$ to $D_0 17b^2$, is occurring. Figure 14(*a*) shows the mass-selected ion-dip spectrum of the *p*-difluorobenzene cation obtained by the above conditions. The spectrum is due to the electronic transition from the $D_0(^2B_{2g})$ ground state to the $D_3(^2B_{3u}, \pi, \pi)$ state. As can be seen from the figure, a well resolved vibrational structure is developed from the strong dip at 23 794 cm^{-1} toward the higher frequency side. The appearance of such a well resolved structure clearly demonstrates that this spectroscopy is very useful in detecting the electronic transition of cations at very low concentration in the gas phase with a high resolution.

Since the ground-state ions produced are exclusively in the $D_0 17b^2$ level, the spectrum of figure 14 must be due to the transition from this level, that is, all the dips in

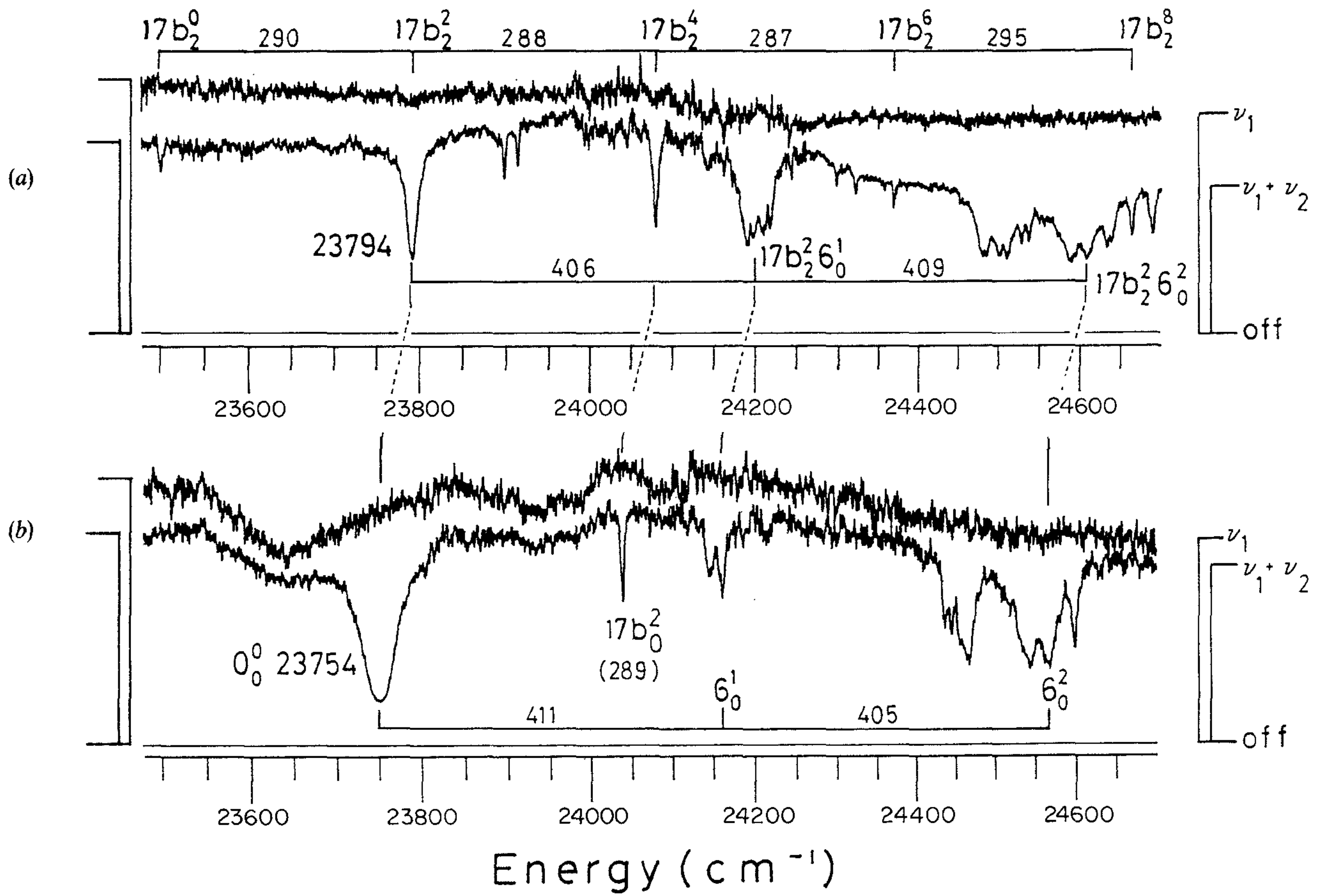

Figure 14. Mass-selected ion dip spectra of jet-cooled *p*-difluorobenzene cation due to the $D_3 \leftarrow D_0 17^2_b$ (*a*) and $D_3 \leftarrow D_0 0^0$ (*b*) transitions. The traces indicated by ν_1, $\nu_1 + \nu_2$ and off represent the signals when ν_1 is on, both ν_1 and ν_2 on and both ν_1 and ν_2 off respectively. In (*b*), ν_2 corresponds to ν_3 in text.

the spectrum are hot bands. Since the Franck–Condon factor will be large for the transition of $\Delta v = 0$, the lowest-frequency strong dip at 23 794 cm^{-1} may be assigned to $D_3 17b^2 \leftarrow D_0 17b^2$. Since we know the ground-state frequency of $17b^2$, the origin band $D_3 0^0 \leftarrow D_0 0^0$ is calculated to be at 23 744 cm^{-1}. This origin can be confirmed when we observe the mass-selected ion-dip spectrum of the $D_0 0^0$ cation, which will be efficiently produced by photo-ionization of the neutral molecules in $S_1 0^0$. However, as mentioned before, when we use $S_1 0^0$ as a resonance state in one-colour resonant enhanced two-photon ionization, we have insufficient energy for the ionization. To achieve the preparation of the $D_0 0^0$ molecules, the $S_1 0^0$ molecules excited by ν_1 were ionized by different laser light of ν_2, whose frequency coincides with the frequency difference between $D_0 0^0$ and $S_1 0^0$. The $D_0 0^0$ molecules thus produced are subject to the measurement of the mass-selected ion-dip spectrum with the third laser light of ν_3. Therefore here we used three different laser lights and it is three-colour spectroscopy. The mass-selected ion-dip spectrum thus obtained is shown in figure 14(*b*) (Y. Tsuchiya, M. Fujii and M. Ito, unpublished work). It is seen that the origin of the $D_3 \leftarrow D_0$ transition appears strongly at 23 754 cm^{-1}, which is exactly the position predicted before. All the dips appearing in the figure are cold bands due to the transitions from $D_0 0^0$. By use of two laser sources of ν_1 and ν_2, it is possible to prepare the D_0 molecules in any particular vibrational level, so as to give the spectrum consisting of hot bands involving this particular ground-state mode. In this way, we can obtain a number of the ion-dip spectra due to the transitions from various vibrational levels in D_0. They provide detailed information on the vibrational levels and potentials of electronic excited states of cations. For the *p*-difluorobenzene cation, Tsuchiya *et al.* measured the ion-dip spectra due to the transitions from six different vibrational levels in D_0 and detailed information on the potential of the D_3 state was obtained. It was found that the potential in D_3 is greatly deformed along a particular out-of-plane coordinate by the vibronic coupling of D_3 with a nearby $D_n(\sigma, \pi)$ state.

Mass-selected ion-dip spectroscopy employing dissociation provides us with useful information not only on the level structure of excited electronic state of a cation but also on the dissociation mechanism of the excited cation. In the case of the *p*-difluorobenzene cation it was found that the $D_3(\pi, \pi)$ state itself is not dissociative, but it does dissociate in a higher excited σ, π state reached by the absorption of another photon. This dissociation mechanism seems to be general for all the benzene derivatives.

6. Concluding remarks

Several two-colour dip spectroscopies recently developed were briefly reviewed. As was demonstrated by application to the examples, the dip spectroscopies are powerful tools for studying the energetics and dynamics of large molecules in their ground, low-lying excited and very highly excited states, and even of ions. In particular, the combination of two-colour dip spectroscopy with the supersonic jet technique greatly simplifies the electronic spectra of large molecules and ions, and provides us with detailed information on energy-level structures and potentials of electronic states which are not accessible by conventional spectroscopic techniques. As was shown in section 5, triple-resonance spectroscopy using three laser beams is already becoming practical, and will create many more useful spectroscopies for the study of the electronic states of molecules and ions.

Acknowledgments

The author thanks N. Mikami, T. Ebata, M. Fujii, T. Suzuki and Y. Tsuchiya for their essential contributions to the work.

References

ANEZAKI, Y., EBATA, T., MIKAMI, N., and ITO, M., 1985, *Chem. Phys.*, **97,** 153.

COOPER, D. E., KLIMBAK, C. M., and WESSEL, J. E., 1981, *Phys. Rev. Lett.*, **46,** 324.

COOPER, D. E., and WESSEL, J. E., 1982, *J. chem. Phys.*, **76,** 2155.

EBATA, T., IMAJO, T., MIKAMI, N., and ITO, M., 1983, *Chem. Phys. Lett.*, **89,** 45.

EBATA, T., MIKAMI, N., and ITO, M., 1983, *J. chem. Phys.*, **78,** 1132.

FUJII, M., EBATA, T., MIKAMI, N., and ITO, M., 1983, *Chem. Phys. Lett.*, **101,** 578; 1984, *J. phys. Chem.*, **88,** 4265.

FUJII, M., MIKAMI, N., and ITO, M., 1985, *Chem. Phys.*, **99,** 193.

FUJII, M., KAKINUMA, T., MIKAMI, N., and ITO, M., 1986, *Chem. Phys. Lett.*, **127,** 297.

GOTO, A., FUJII, M., MIKAMI, N., and ITO, M., 1985, *Chem. Phys. Lett.*, **119,** 17.

GOTO, A., FUJII, M., and ITO, M., 1987a, *Chem. Phys. Lett.*, **135,** 407; 1987b, *J. phys. Chem.*, **91,** 2268.

HARTREE, D. R., 1928, *Proc. Camb. Phil. Soc.*, **24,** 426.

HUNT, G. R., and ROSS, I. G., 1962, *J. molec. Spectrosc.*, **9,** 50.

ITO, M., 1986, *Vibrational Spectra and Structure*, Vol. 15, edited by J. R. Durig (Amsterdam: Elsevier) p. 1.

ITO, M., EBATA, T., and MIKAMI, N., 1988, *Ann. Rev. phys. Chem.*, **39,** 123.

ITO, M., and FUJII, M., 1987, *Advances in Multi-photon Processes and Spectroscopy*, Vol. 4, edited by S. H. Lin (Singapore: World Scientific), p. 1.

KAKINUMA, T., FUJII, M., and ITO, M., 1987, *Chem. Phys. Lett.*, **140,** 427.

KAKOSCHKE, R., BOESL, U., HERMAN, J., and SCHLAG, E. W., 1985, *Chem. Phys. Lett.*, **119,** 467.

KAMINSKY, M. E., HAWKINS, R. T., KOWALSKI, F. V., and SCHAWLOW, A. L., 1976, *Phys. Rev. Lett.*, **36,** 671.

KITTREL, C., ABRAMSON, E., KINSEY, J., MCDONALD, S. A., REISNER, D. E., FIELD, R., and KATAYAMA, D. H., 1981, *J. chem Phys.*, **75,** 2056.

MURAKAMI, J., KAYA, K., and ITO, M., 1982, *Chem. Phys. Lett.*, **91,** 401.

NEUSSER, H. J., 1987, *Int. J. Mass Spectr. Ion Prod.*, **79,** 141.

RIPOCHE, X., DIMICOLI, I., LE CALVE, J., PUIZZI, F., and BOTTER, R., 1988, *Chem. Phys.*, **124,** 305.

SUZUKI, T., HIROI, M., and ITO, M., 1988, *J. phys. Chem.*, **92,** 3774.

SUZUKI, T., and ITO, M., 1987, *J. phys. Chem.*, **91,** 3537.

SUZUKI, T., MIKAMI, N., and ITO, M., 1986, *J. phys. Chem.*, **90,** 6431.

SYAGE, J. A., and WESSEL, J. E., 1987, *J. chem. Phys.*, **87,** 3313.

TSUCHIYA, Y., FUJII, M., and ITO, M., 1989, *J. chem. Phys.*, **90,** 6965.

VACCARO, J., KINSEY, J., FIELD, R., and DAI, H. L., 1983, *J. chem. Phys.*, **78,** 3659.

WALTER, K., WEINKAUF, R., BOESL, U., and SCHLAG, E. W., 1988, *J. chem. Phys.*, **89,** 1914; 1989, *Chem. Phys. Lett.*, **155,** 8.

WEINKAUF, R., WALTER, K., BOESL, U., and SCHLAG, E. W., 1987, *Chem. Phys. Lett.*, **141,** 267.