Journal of Molecular Structure, 173 (1988) 201-213
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HIGH RESOLUTION LASER SPECTROSCOPY AS A TOOL TO INVESTIGATE DYNAMICS IN LARGE MOLECULES AND MOLECULAR CLUSTERS

W. Leo Meerts and W.M. van Herpen
Fysisch Laboratorium, University of Nijmegen, Toernooiveld,
6525 ED Nijmegen, The Netherlands.

1. ABSTRACT

Much information on the dynamical and structural properties of electronically excited states can be substracted from (ultra) high resolution laser spectroscopy with MHz resolution. This is demonstrated on the radiationless transitions from the first excited singlet state in pyrazine and the spectra of tetracene and its van der Waals complexes with noble gases. In both systems the existence of interstate coupling is clearly observable, while in pyrazine the individual molecular eigenstates have been studied in the frequency and in the time domain.

2. INTRODUCTION

Detailed spectroscopic information is indispensible in the study of structure, binding energies and dynamic behaviour of large molecules and van der Waals (vdW) complexes. Experimental data allow for a realistic description of potential energy surfaces and relaxation phenomena, among which the radiationless transitions such as internal conversion (IC) and intersystem crossings (ISC) form an important category. Unfortunately the density of states is rapidly increasing in larger molecules and vdW clusters and so does the complexity of the spectra. Doppler-free techniques in cells (ref. 1) can be used to some extent to improve the resolution, however the relatively high temperature give rise to an enormous amount of spectral lines. An experimental set-up with a free jet expansion of the molecules in a seeding gas considerably improves the situation. In this way, a cooling of the internal degrees of freedom of the molecules is accomplished, which results in a substantial reduction of the number of observed transitions. Moreover, vdW complexes are readily formed in the expansion.

0022-2860/88/$03.50

If laser excitation occurs directly behind the nozzle the spectral resolution is sufficient to observe vibrational structure and even rotational transitions with unresolved K-structure (ref. 2). The resolution can be increased considerably by enlarging the distance between the nozzle and the laser excitation area and simultaneously strongly reducing the divergence of the molecular beam. The experimental linewidth is reduced to several MHz in the visible and near UV region if at the same time a continuous wave (cw) single mode laser is employed (ref. 3). In the present paper it will be shown that such high resolution is needed to reveal the individual molecular eigenstates (ME) in a molecule like pyrazine. Pulsed amplitude modulation of the single frequency laser radiation allowed the observation of radiative lifetimes of individual ME´s. A combination of the frequency and time domain spectra made it possible to get a good understanding of the non-radiative decay processes that take place in the S_1 state of the pyrazine molecule.

A discussion will also be given on the rotationally resolved spectra of tetracene (T) and its vdW complexes with argon, krypton and xenon. The rotational band of the free molecule gives insight in its structure. It has been found before (ref. 4) that vibrational excitation in the S_1 state, 1600 cm^{-1} above the ground vibrational level, shows a shortening of the decay lifetime. This effect has been attributed either to the S_1-T intersystem crossing or to the S_1-S_0 internal conversion. A high resolution investigation allowed us to study such interactions, even near the electronic origin of the S_1 state. It was found that such interstate couplings, although weak, show up in the regime of low vibrational energies in T. It was furthermore found that these effects are enhanced in the vdW complexes. The increased interstate coupling is in agreement with lifetime measurements made at vibrational resolution (ref. 5), where the decay lifetimes of the T-noble gas complexes decreased rapidly in the order argon, krypton and xenon.

3. EXPERIMENTAL SET-UP

In order to obtain MHz resolution in the visible and near UV part of the spectrum we have used the molecular beam set-up in combination with single frequency dye lasers. The apparatus was described in detail elsewhere (ref. 3-6) and only a brief description of the most relevant features is given here. The sample was seeded with a noble gas, mostly argon, and expanded through a continuous nozzle (100 μm diameter) at backing pressures between 0.5 and 1 atm in a vacuum chamber. The source was either kept at room temperature or heated to about 200 °C (for tetracene) and the rotational temperatures are estimated to be about 3 K. The molecular beam was strongly collimated by two conical skimmers. This resulted in a residual Doppler width of 10-15 MHz. The interaction zone with the laser is at 30 cm from the beam orifice. Here the undispersed laser induced fluorescence is detected with a photomultiplier.

Two different laser systems have been applied. The measurement on the tetracene molecule in the blue part of the spectrum have been performed with a standing wave linear dye laser (Coherent Radiation 591). In the near UV we used a frequency doubled modified ring dye laser (Spectra Physics 380D). The doubling crystal, made of $LiIO_3$, was placed intracavity and angle tuned (ref. 7). Both lasers operated single frequency with a bandwidth below 3 MHz.

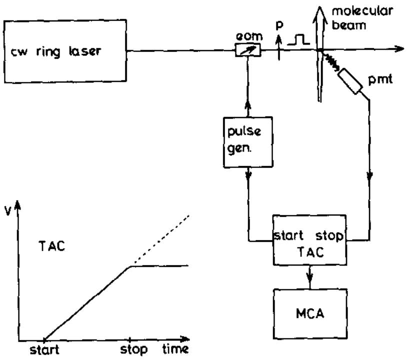

Fig. 1. Scheme of the set-up used in the single photon counting for the lifetime measurements. Here eom stands for electo optic modulator, pmt for photomultiplier tube, TAC for time to amplitude converter and MCA for multi-channel analizer.

For the lifetime measurements the laser was held on the peak of a single transition, while the laser radiation was modulated with an electro-optic modulator (Coherent Radiation) in conjunction with a polarizer. This resulted in single frequency pulses of 40 ns duration with a light on-off ratio of about 150. The repetition rate was 12 kHz. The photons emitted upon excitation were detected using a single photon counting technique. The schematics of the set-up is shown in fig. 1. Pile up was prohibited by a pile-up inhibitor. The strongest lines yielded about 0.1 photon per shot.

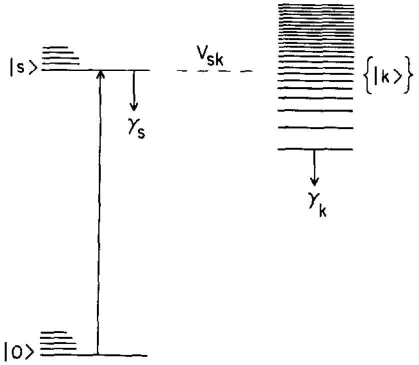

Fig. 2. Energy level scheme of a "large molecule".

4. RADIATIONLESS TRANSITIONS IN PYRAZINE

A radiationless transition is defined as a change in the electronic state of a molecule without the absorption or emission of radiation. In bound states there are two processes of this type, internal conversion and intersystem crossing. The first is a transition between states of the same multiplicity, whereas the second is a transition between states of different multiplicity. Following the absorption of light many organic molecules were found to have emission quantum yield less than unity. The observed radiative lifetimes are often considerably shorter than values calculated from integrated absorption coefficients, while most molecules excited to a higher electronic state emit light only from a lower electronic state. Non-radiative transitions require the excistence of compound or mixed states, consisting of a superpostion of eigenstates of the total Hamiltionan, since for example a molecular system in a stationary state cannot be induced to make transitions in the absence of a radiation field. In a broader sense, radiationless transitions are related to transfer of energy from one part of a multidimensional potential energy surface to another. Since the energy must be conserved in a non-radiative process, other degrees of freedom must play a role, thereby establishing a connection between radiationless transitions and intermolecular dynamics.

Radiationless transition theory (ref. 8-11) is usually presented in terms of an initial level |0> before excitation, a zero order level |s> that is prepared by the excitation, and a dense manifold of final levels {|k>} into which the level |s> can decay.

Figure 2 depicts schematically the energy level scheme of a large molecule in the region of the initially excited state $|s\rangle$, with a natural energy uncertainty γ_s. Isoenergetic with $|s\rangle$ is a manifold of rovibrational levels of a lower excited state or the ground electronic state. The zero order levels $\{|k\rangle\}$, each with an energy uncertainty γ_k, interact with the level $|s\rangle$ via off-diagonal terms in the molecular Hamiltonian of magnitude v_{sk}.

Several cases can now be distinguished depending on the strength of the coupling v_{sk} and the density of states $\{|k\rangle\}$: the small molecule limit, the statistical limit and the so-called intermediate state case (ref. 9). We will concentrate on the latter one, since all the experimentally observed phenomena in pyrazine can be explained adopting this model. In the intermediate case limit only a relatively small number, between 10 and 1000, of the $\{|k\rangle\}$ manifold of states are coupled to the prepared state $|s\rangle$. If the sparse manifold, containing the state $|s\rangle$, is prepared with a few nanosecond pulsed light source, it is expected that the decay process of the $|s\rangle$ state is non-exponential. Quantum beats may also be observed. Non-exponential decays have been observed for the first time by Frad et al. (ref. 12) in bulb experiments and by many investigators in supersonic jet work (see for example references cited in ref. 13). Quantum beats were for the first time found by ter Horst et al. (ref. 2) in a supersonic jet experiment. Both a non-exponential decay behaviour and the excistence of quantum beats demonstrate in an indirect way the intermediate state case in the pyrazine molecule. Indirect, because the interpretation of the experimental observation heavily leans on a simplified theoretical model.

An unambiguous, model independent, solution to this problem requires the observation of the actual spectrum fully resolved in the predicted mixed states and showing that the Fourier transformation of these states into the time domain produces a decay that agrees with the experiment. Supersonic jet experiments although able to show partially resolved rotational spectra (see for example ref. 14) are not capable to resolve the individual ME´s. In order to observe these ME´s in molecules like pyrazine we had to apply the (ultra) high resolution spectroscopy as discussed in the present paper. Figure 3 shows the result (ref. 15-16) for the P(1) of the $^1B_{3u} \leftarrow ^1A_g$ transition in pyrazine. Since this transition accesses the J´=0, K´=0 state it would consist of a single line if the electronic transition was between two ordinary singlet states. The observed splittings in this spectrum are a direct proof for the excistence of the ME´s and allows the study of their properties. At first the density of states to which $|s\rangle$ couples can simply be obtained by counting the number of transitions. The result is 150 /cm^{-1}. This is sufficiently sparse that only a limited number of ME´s are contained within the coherence width of a pulsed light source. The observed decay will then depend on the time duration of the source, which accounts for the widely varying decay behaviour reported in the literature (see references cited in ref. 13).

Secondly from the intensities and frequency positions one can, under the assumption that the intensities of the observed excitation spectrum are proportional to those of the absorption spectrum, deduce both the strength of the coupling (v_{sk}) between the state $|s\rangle$ and the $\{|k\rangle\}$ manifold as well as the "zero order" energies of these states. This can be achieved using a dediagonalization either by a trial and error method (ref. 15) or more elegantly with the help of Green´s functions (ref. 17). The result of this procedure shows that the common assumption in the theory of radiationless transitions, that the coupling matrixelements are relatively constant, is incorrect. The values of v_{sk} span nearly an order of magnitude, from 50 to 500 MHz.

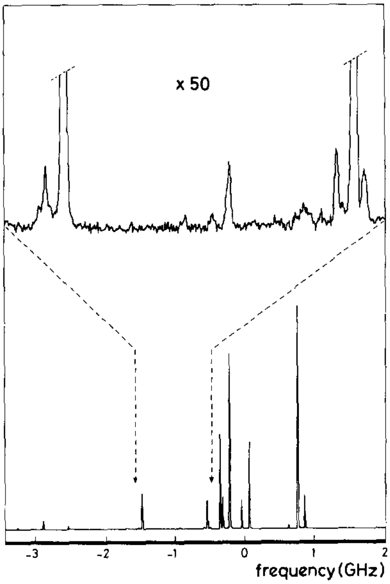

Fig. 3. The molecular eigenstate spectrum of the P(1) transition in pyrazine. ν = −12192 MHz relative to the origin of the $^1B_{3u} \leftarrow {}^1A_g$ electronic transition.

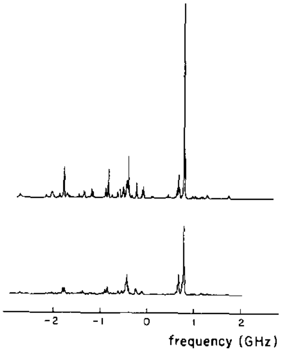

Fig. 4. The P(3) molecular eigenstate spectrum of pyrazine in zero field (top) and in a field of 30 G. Both spectra were recorded at the same absolute intensity level.

By applying a small magnetic field in the detection region it is possible to learn something more about the nature of the coupling. As expected for a J′=0 state, the P(1) transition shows only a weak field dependence. However all the spectra for J′≠0 are strongly perturbed by fields of several tens of gauss. Figure 4 shows the P(3) transition as an example. The dramatic change in relative intensities demonstates that the dominant nature of the states that are coupled to |s> must be of triplet character.

As mentioned above the dediagonalization of the ME spectrum can only be performed correctly in the case that the excitation spectrum is proportinal to the absorption spectrum. This is equivalent to the fact that the decay channel is dominated by the singlet decay ($\gamma_s \gg \gamma_k$). From the observation of the lifetimes of the individual molecular eigenstates in the high resolution experiment, we have found (ref. 16) that this is incorrect. In this experiment it was shown that excitation to a single ME state in the P(1) transition gives rise to a single exponential decay (fig 5). Further it was found that the |s> state of pyrazine has significant radiationless decay channels to the zero order triplet states and/or highly vibrationally excited states of the singlet electronic ground state.

Let us now briefly discuss what the combination of jet spectra and the high resolution spectra can teach us about the non-radiative processes that take place in pyrazine. For this purpose we consider the model (ref. 9,18-20) depicted in figure 6. Two type of zero-order triplet levels are assumed, {|t>} and {|t′>}, as well as a high density of highly vibrationally excited electronic ground state levels {|s′>}.

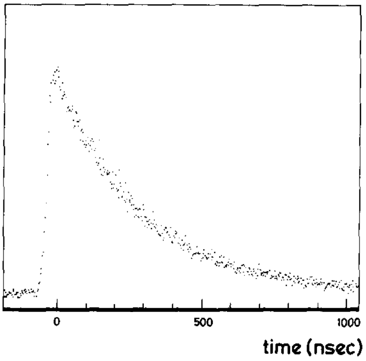

Fig. 5. Decay curve of a single ME state in the P(1) spectrum of pyrazine.

The set {|t>} is strongly coupled to |s> yielding the mixed levels {|st>} that carry most of the oscillator strength to |0>. These levels are resposible for the strong lines in the high resolution spectra. The levels {|t'>} and/or {|s'>} are only weakly coupled to {|st>}, but their density is much higher than the density of the {|st>} levels. This gives rise to weaker lines and/or a continuous background in the high resolution spectra. Non-vanishing matrixelements of a Coriolis interaction are held mainly responsible for the coupling between {|st>} and {|t'>}, {|s'>}. Such an interaction, small for the P(1) transition but increasing with J, explains the decrease of the quantum yield with increasing J-state (ref. 19,21).

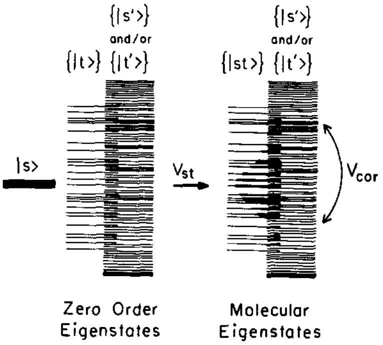

Fig 6. Model for the interelectronic state coupling near the S_1 origin of pyrazine. After Knight et al. (ref 20).

5. SPECTROSCOPY OF TETRACENE AND ITS VAN DER WAALS COMPLEXES

In tetracene we have studied (ref. 22) three of the lowest vibrational states (0, 311 cm^{-1} and 471 cm^{-1}) in the S_1 electronic state by observing the high resolution laser excitation spectrum around 22000 cm^{-1}. Because of the fact that the molecule is so heavy even at high resolution the density of rotational transitions is very high. A typical spectrum is shown in figure 7. The linewidth in these spectra is 15 MHz and is determined by the residual Doppler width of the spectrometer. This is in agreement with the decay lifetime measurements of the excited state (ref. 2). Figure 7 also shows the calculated spectrum using an asymmetric rotor model. What should be noted is that both the frequencies and intensities of all observed spectral features are explained and are attributed to pure rotational transitions. Both the 0-0 and the 311 cm^{-1} transition are of perpendicular type. Furthermore the experimental spectra show a noticeable background of the order of 20 % of the intensities of single lines. This point will be discussed in more detail below.

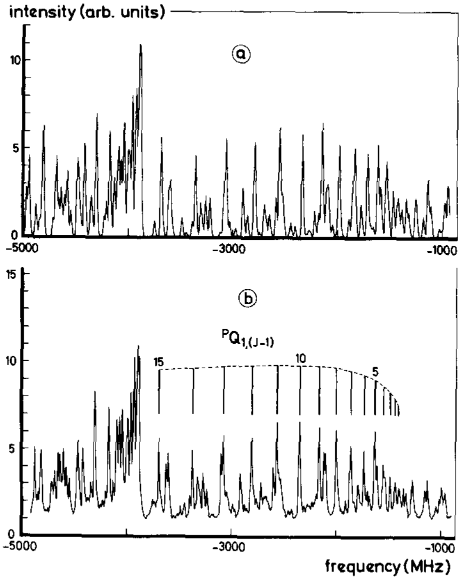

Fig. 7. Part of the 0-0 rotationally split perpendicular band around ν_0 = 22396 cm^{-1} of tetracene. The upper spectrum (a) is the calculated one, while (b) is the observed one.

In the complex of T with argon we have observed those transitions which are corresponding to the 0-0, 311 cm^{-1} and 471 cm^{-1} bands in the parent T molecule. The overal appearence was as can be expected: a perpendicular type rotational transition for the first two and a parallel for the last one. The spectra of the perpendicular bands show a characteristic shape with pronounced Q branches. It should be noted that this structure is on a broad background, which is quite a bit larger than in the T molecule.

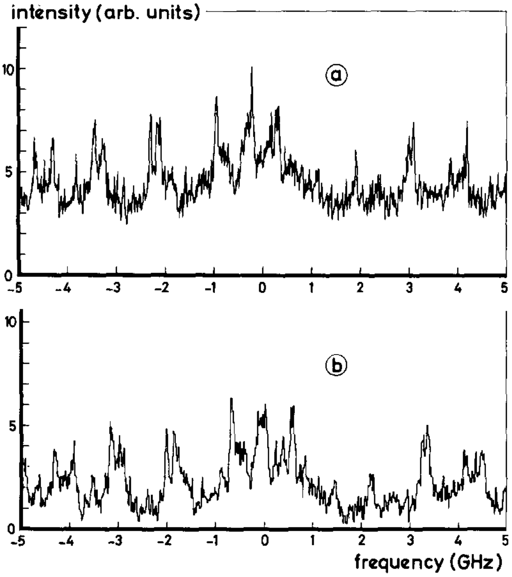

Fig. 8. The observed 0-0 (b) and 311 cm^{-1} (a) rovibronic bands of the tetracene-argon vdW complex.

Because of the high density of states no single spectral lines are observed and it is difficult to estimate the exact linewidth. We assume that it is still Doppler limited. Unfortunately, we did not succeed in assigning the rotational spectra of the T-Ar vdW complex. As this molecule has very small rotational constants, the spectra are extremely dense, even at a 15 MHz linewidth. On the basis of the experimental resolution it should still be possible to resolve and assign the rotational bands of a molecule as large as the T-Ar complex. Despite much effort, such an assignment could not be found. For example the clear sequence of the Q branches in the perpendicular bands looks distorted. In the parallel band there seems to be an excess of lines. Although there is no incontestable proof, we are convinced that the appearence of extra lines is, like in pyrazine, due to perturbations in the rotational spectrum. This is even more evident if one looks at the spectra of the T-Kr complex.

In figure 9 we see that the two observed transitions in T-Kr have hardly any resemblance, although they correspond to the same ones as observed in T-Ar (fig 8). The 0-0 spectrum in T-Kr extends over a broad region of more than 100 GHz and suggests the presence of two transitions. There is a pronounced Q-like branch, typically for a parallel band, and at a distance of about 4 GHz, a number of smaller Q-branches, characteristic for a perpendicular transition. Individual spectral lines are no longer observed. The 311 cm^{-1} vibronic transition shows an unrecognizable structure of some broad shallow patterns. Again the background in the spectra of T-Kr should be noted. The expected linewidth on basis of the measured lifetime (ref. 4) is about 25 MHz and exceeds the residual Doppler width.

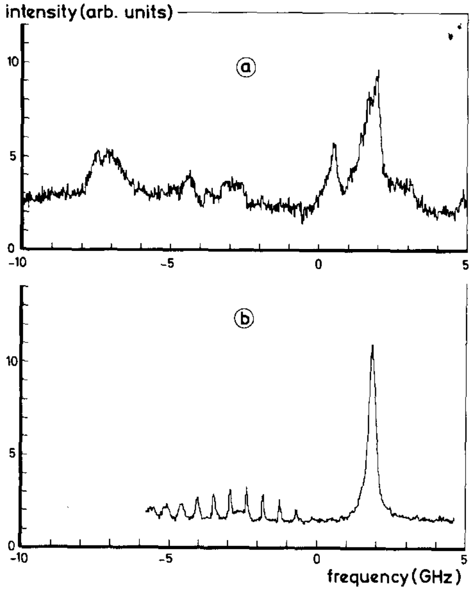

Fig. 9. The observed 0-0 (b) and 311 cm^{-1} (a) rovibronic bands of the tetracene-krypton vdW complex.

The 0-0 rovibronic band of the T-Xe complex shows even less structure than the T-Kr spectra. Now there also exist a broad (>100 GHz) background with only some humps as structure in a 30 GHz region. No trace of individual lines has been observed, so the natural linewidth in the spectrum must be of considerable size. The decay lifetime has been esimated (ref. 5) to be 1.5 ns, corresponding to a linewidth of 100 MHz.

All the spectra of the complexes studied have two characteristics in common: i) Too many spectral lines and/or unresolved, with increasing complexibility from argon to xenon, ii) a structureless background of several cm^{-1} wide. Of the possible explanations for these observation such as spectra from isotopic species, weak underlying bands, all observations are consistent with the assumption of ISC and/or IC interactions. Because of the very high density of rotational levels in tetracene and its complexes, we might expect that the extra lines arising from the mixed ME´s will overlap. This overlap is increasing going from tetracene to tetracene bound to noble gases with increasing weight, which indicates that the interstate couplings increase in the same order.

6. CONCLUSIONS

It has been demonstrated that high resolution spectroscopy presents a valuable tool, which reveals much of the photo dynamical processes that take place in large molecules. Two special cases have been discussed in detail: the intermediate case in pyrazine and the statistical limit case in tetracene. In some respects however the first molecule behaves as a small molecule (ref. 13), while the latter one shows features of an intermediate case.

7. ACKNOWLEDGEMENTS

The authors would like to thank dr. W.A. Majewski, prof D.W. Pratt and prof. J. Kommandeur for many stimulating discussions. Prof. A. Dymanus is ackowledged for his continuing interest in the problem. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and has been made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk onderzoek (ZWO).

8. REFERENCES

1. E. Riedle, H.J. Neusser and E.W. Schlag, J.Chem. Phys. 75 (1981) 4231-4240.
2. G. ter Horst, D.W. Pratt and J. Kommandeur. J.Chem.Phys. 74 (1981) 3616-3618.
3. W.Majewski and W.L. Meerts, J.Mol.Spectrosc. 104 (1984) 271-281.
4. A.Amirav, U.Even and J. Jortner, J.Chem. Phys. 75 (1981) 3770-3793.
5. A.Amirav, U.Even and J. Jortner, J.Chem. Phys. 75 (1981) 2489-2512.
6. J.P. Bekooy, W.L. Meerts and A. Dymanus. J.Mol.Spectrosc. 102 (1983) 320-343
7. W. Majewski, Opt. Comm. 45 (1983) 201-206.
8. M. Bixon and J. Jortner, J.Chem.Phys. 48 (1968) 715-726; J.Chem.Phys. 50 (1969) 3284-3290 and 4061-4070.
9. A.Tramer and R. Voltz, Excited states, E.C. Lim (Editor), Academic, New York, 1978, pp 281-394.
10. W.Rhodes, Radiationless transitions, S.-H. Lin (Editor), Academic, New York, 1980, pp 219-258.
11. Ph. Avouris, W.M. Gelbart and M.A. El-Sayed, Chem Rev 77 (1977) 793-833.
12. A.Frad, F.Lahmani, A. Tramer and C.Tric, J.Chem.Phys 60 (1974) 4419-4430.
13. J. Kommandeur, W.A. Majewski, W.L. Meerts and D.W. Pratt, Ann.Rev. Phys.Chem. 38 1987) 433-462.
14. Y.Matsumoto, L.H.Spranger and D.W. Pratt, Laser Chem. 2 (1883) 91-114.
15. B.J. van der Meer, H.Th. Jonkman, J. Kommandeur, W.L. Meerts and W.A. Majewski, Chem.Phys.Lett. 92 (1982) 565-569
16. W.M. van Herpen, W.L. Meerts, K.E. Drabe and J. Kommandeur, J.Chem.Phys. 86 (1987) 4396-4400.
17. W.D. Lawrence and A.E.W. Knight, J.Phys.Chem. 89 (1985) 917-925
18. Y.Matsumoto, L.H. Sprangler and D.H. Pratt, J.Chem.Phys. 80 (1984) 5539-5544.
19. P.J. de Lange, B.J. van der Meer, K.E. Drabe, J. Kommandeur, W.L. Meerts and W.A. Majewski, J.Chem.Phys. 86 (1987) 4004-4010.
20. A.E.W. Knight, J.T. Jones and C.S. Parmenter, J.Chem.Phys. 87 (1983) 973-983.
21. A.Amirav and J.Jortner, J.Chem.Phys. 84 (1986) 1500-1507.
22. W.M. van Herpen, W.L. Meerts and A. Dymanus, J.Chem.Phys. 87 (1987) 182-190.