Cluster spectroscopy

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CLUSTER SPECTROSCOPY

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1. Introduction

This review for non-specialists begins with two general statements. First, cluster spectroscopy does not exist, at least if one agrees to consider loosely bound complexes of more than two, three or possibly four molecules as clusters. Being invited to talk about cluster spectroscopy one has to restrict oneself mainly to dimer spectroscopy, e.g. fluorene-Ar, H_2-Ne, $(C_2H_4)_2$, etc. The second statement is that dimer spectroscopy does exist, but has brought us at least as many problems as solutions to problems. This is especially true for the i.r. spectroscopy of the pre-dissociation of dimers.

In the following, the main emphasis will be put on pre-dissociation of dimers in a molecular beam which is irradiated by i.r. lasers, e.g. CO_2-lasers or colour center lasers. Pre-dissociation spectra generally yield broad lines with little or no structure; with respect to the monomer band origines there occur apparently random lineshifts to the blue and/or to the red, which we shall try to explain.

Before we start with the discussion of these phenomena an example of each, an electronic excitation spectrum, a RF-spectrum, an i.r. spectrum and a Raman spectrum of a dimer, will be discussed, together with a summary of the information residing in these spectra

2. Examples

The example of electronic UV-excitation is concerned with fluorene-Ar; in Fig. 1 its excitation spectrum is depicted (ref. 1). Note the exceptionally high resolution (35 MHz fwhm) which is obtained in spite of the fact that the excited state may have been expected to dissociate. On the other hand, fluorene complexes with two Ar atoms don't show sharp structures, presumably because here dissociation is a very fast process, see the pioneering work of the Chicago group (ref. 2). It is from the rotational analysis that the structure of the dimer has been determined.
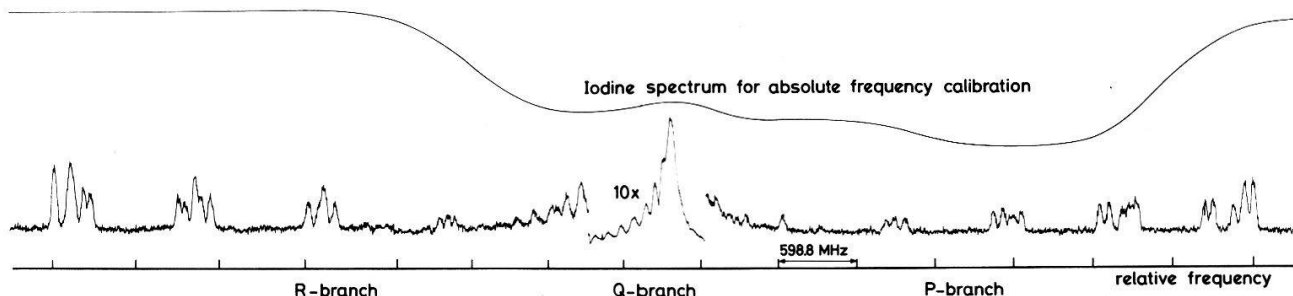
Figure 1

The fluorescence spectrum of fluorene-Ar ($C_{13}H_{10}$ - Ar), vs. the exciting
laser frequency around λ = 296 nm. The P and R-branches split for increasing
J-values, because the K-degeneracies are lifted for this slightly asymmetric
prolate top. Note the high resolution achieved, due to which the rotational
structure has been resolved completely. Of the measured spectrum, which ex-
tends over all J $\lesssim$ 15 values, only the region with J $\leq$ 4 is shown here. The
frequency increases from right to left. To remain within the graph, the strong
Q-branch has been attenuated with a factor 10 compared to the rest of the
spectrum.

        Change of state by absorption/emission of RF-frequencies leaves
dimers in the stable ground state, i.e. linewidths arise from conventional
effects. In a molecular beam measurement time of flight – broadening dominates
and often allows to determine transition frequencies with an uncertainty of
about 100 Hz, e.g. for H_2-Ar (ref. 3). If, on the other hand, i.r. bulk
absorption measurements are performed, for the same system, pressure broaden-
ing limits the linewidth to about 3 GHz (ref. 4). For HD-Ar, pre-dissociation
effects yield a linewidth of about 15 GHz, depending on the end-over-end
rotational quantum number and in fair agreement with theory (ref. 5).

        Absorption of i.r. frequencies leads to excitation of a vibrational
mode of one cluster constituent. The energy deposited in such a mode exceeds

by far the dissociation energy of a cluster. Moreover, the vibrational motion
is normally strongly coupled to the v.d. Waals-stretch-mode (or similar clus-
ter modes). In contrast to the electronic excitation spectrum (Fig. 1) life-
time effects strongly limit the resolution of the obtained spectra, whether
they are obtained under molecular beam conditions or in bulk. In ref. 6, bulk
measurements on N_2-N_2 are reported, with linewidths of about 150 GHz, whereas
in a molecular beam $(C_2H_4)_2$ excitation led to a linewidth of ca. 300 GHz
(ref. 7-11).

       $(Ar)_2$ Raman spectra were published in ref. 12. This technique looks
promising as it yields resolved rotational and vibrational structures.

3. General features

       The following general features emerge from the examples mentioned.
A) The v.d. Waals-stretch vibration and similar internal motions have absorp-
   tion frequencies of about $10 \div 50$ cm^{-1}; they were resolved in Raman spectra
   (ref. 12) and in bulk i.r. absorption spectra (e.g. ref. 6). Almost free
   internal rotation of the molecular constituents of the dimer shows nearly
   equidistant rotational lines which have been resolved in i.r. bulk absorp-
   tion measurements, e.g. for rotational quantum numbers of N_2 up to about
   $j = 10$ (see ref. 6).
B) End-over-end rotations show typical spacings smaller than about 0.1 cm^{-1}.
   For hydrogen-rare gas complexes they are clearly resolved by i.r. bulk
   absorption measurements (ref. 4). Direct micro-wave measurements, too,
   on molecular beams have been performed succesfully (ref. $13 \div 15$).
C. Hyperfine structure analysis of dimers has been developed by the Harvard
   group and others; it has become a major tool for the determination of
   structure of and molecular interactions within dimers (ref. 16).

4. Molecular beam i.r. pre-dissociation measurements

       Relatively new and unexploited so far are i.r. pre-dissociation
measurements in molecular beams, first attempted by the Waterloo group (ref.
17). Due to beam cooling only a few states are occupied, limiting the amount
of information. Neither do quasi-band states (directly observed in bulk) con-
tribute to these spectra. Normally broad single lines or scarcely structured
lines have been observed; the main information in store consists of the line-

width – connected to the lifetime of the excited state – and the line shift
with respect to the position for the monomer.

In addition, i.r. pre-dissociation measurements yield information
on the kinetic energy of the fragments and allow an indirect determination of
the internal energy still residing in the fragments; in ref. 7, 8 and 18
about 10% or less of the available energy is reported to appear in the kinetic
fragment energy.(From dispersed LIF measurements, for electronic excitation
this energy redistribution has been measured directly, for many molecules
(ref. 2, 19, 20 and 21)).

5. The experimental method of i.r. predissociation measurements

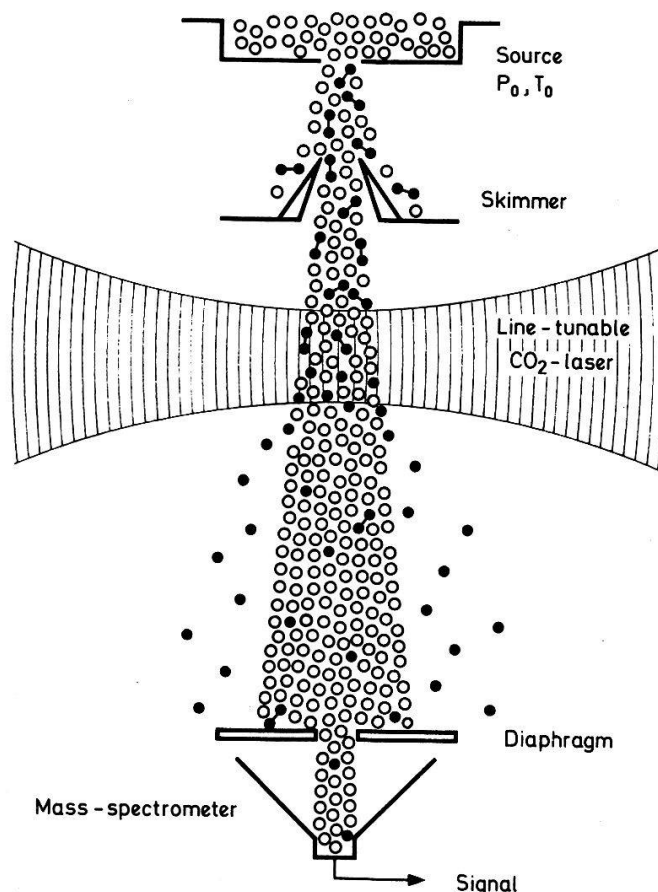In fig. 2 the straightforward experimental set-up, with which i.r.

Figure 2

Experimental arrangement. A nozzle beam containing dimers is crossed by a
(line) tunable i.r. laser. The frequency dependence of the attenuation signal
of the mass-spectrometer detector effects the pre-dissociation spectrum of
the dimers.

pre-dissociation spectra have been obtained, is sketched. The molecular beam contains dimers and larger clusters which dissociate as a consequence of the absorption of a vibrational quantum from the CO_2-laser beam. The frequency can be changed in little jumps of about 1.5 cm^{-1}, choosing different lines of the CO_2-laser. With different isotopic mixtures or with a N_2O-filling the number of fixed frequency points can be increased considerably. However, as mentioned above, normally the spectral structures are broader than the spacing between two CO_2-laser frequencies. The detection takes place on the mass spectrometer signal; on the axis an attenuation is observed as consequence of the cluster dissociation.

Historically, the first spectra obtained were measured by bolometric detection of an attenuated $(N_2O)_2$-dimer signal, dissociated by radiation with a continuously tunable colour center laser (ref. 17). (This technique, by the way, allows an accurate determination of the excitation spectrum of the monomer, too). A two-maxima spectrum was found, with peaks at 2233 cm^{-1} and 2246 cm^{-1}, with linewidths of about 10 cm^{-1}, fwhm. The relative strength of the peaks was found 4 : 1. In a first attempt is was suggested that the smaller (blue) peak was due to a combined excitation of the molecular ν_3-mode and a v.d. Waals libration mode of the two N_2O-molecules. For $(OCS)_2$ the excitation-pre-dissociation spectrum was published recently, for frequencies near the $2\nu_5$-band at 1047 cm^{-1} (ref. 8). A single line was found at 1044.7 cm^{-1} with a width of 4 cm^{-1}, fwhm. The dimers were excited with a line tunable CO_2-laser. These are typical examples of results that can be obtained with this method.

6. Results and discussion; i.r. pre-dissociation spectra with clearly resolved structure

In presenting i.r. pre-dissociation results from molecular beam experiments we distinguish between a group of spectra with large splittings and the majority of spectra with unresolved structure.

To the first group belong measurements of $(SF_6)_2$, $(SF_6)_2$-Ar_n and $(SiF_4)_2$. Due to the high symmetry of the molecules involved and the excitation of the threefold degenerate vibrational mode the transitional dipole-moment has no preferential direction within the molecule. Consequently, the vibration can be considered as being decoupled from the rotation, in good approximation. The excited dimer $SF_6^{\dagger} \cdot SF_6$ shows, thus, strong effects due to resonant dipole-dipole forces, with two i.r. active in-phase vibrations: one along the inter-

molecular axis and the other perpendicular to it; to these eigenstates belong a negative energy shift (-2Δ) and a positive one (Δ), respectively (ref. 22, 23 and 24). The total splitting between the two peaks was found to be $3\Delta = 20$ cm^{-1} and has been qualitatively traced back to the resonant dipole-dipole interaction mentioned.

If the $(SF_6)_2$-complex is loaded with Ar-atoms, this double peak feature is preserved, although broadened and red-shifted (ref. 24). Here really large clusters have been investigated; their spectra become similar to those found in matrix spectroscopy (ref. 25 and 26).

For $(SiF_4)_2$ the situation is similar as for $(SF_6)_2$; unfortunately, the maximum of the red peak so far has escaped observation as no CO_2-laser lines were available below 1019 cm^{-1}. However, the expected blue-shifted line has been found leading to $<\mu_{12}^2/4\pi\varepsilon_o R^3 hc> \approx 7$ cm^{-1} (ref. 27). The corresponding value for $(SF_6)_2$ also was about 7 cm^{-1} (ref. 23).

For CF_3Br the tetraeder structure is nearly perfect, but here the excited mode is not threefold degenerate. In accordance no big splitting due to decoupled resonant dipole-dipole forces has been observed (ref. 27).

7. Results and discussion; unresolved i.r. pre-dissociation spectra of $(C_2H_4)_2$

The dimers $(C_2H_4)_2$, $(OCS)_2$, $(CO_2)_2$ and $(N_2O)_2$ fall into the second group with (nearly) unstructured pre-dissociation spectra. The experimental results are summarized in table 1. In the third column the observed shifts are

Table I. Line shifts in dimers. The unshifted position corresponds to the band origin for the free molecule. Shift and line-width are observed for the dimer system indicated.

system	unshifted position (cm^{-1})	shift (cm^{-1})	linewidth (cm^{-1})	neighbouring line(s)	ref.
$C_2H_4(\nu_7) - C_2H_4$	948.8 (b_{1u})	+4	11	$\nu_8 = 9377$ cm^{-1} (b_{2g})	27
$OCS(2\nu_2) - OCS$	1047.04 (Σ^+)	-2.3	4	$\nu_1 = 859$ (Σ^+)	8
$CO_2(\nu_1 + \nu_3) - CO_2$	3716 (Σ_g^+)	-1.2	1.6	$2\nu_2 + \nu_3 = 3609$ (Σ_g^+)	35
$N_2O(\nu_3) - N_2O$	2223.5 (Σ^+)	+10	10	$2\nu_2 + \nu_1 = 2461$ (Σ^+)	17

displayed; they are as often to the blue as to the red side. All shifts are due to Fermi-resonances which can be switched on by the presence of the dimer partner (upper row) or be diminished (lower three rows) (ref. 28).

The free molecule C_2H_4 has two mode frequencies very near to each-other, $\nu_7 = 948.8$ cm^{-1} (b_{1u}, i.r. active) and $\nu_8 = 937.7$ cm^{-1} (b_{2g}, Raman active). The last value has been measured recently in our lab, because no reliable value could be found in literature (ref. 29). The two modes, ν_7 and ν_8, have different symmetry; consequently, matrix elements leading to a Fermi-resonance are absent. However, the dimer-partner slightly perturbs the symmetry with its molecular interaction and gives rise to a Fermi-resonance and subsequent blue shift of the 949 cm^{-1} absorption peak (ref. 7, 8, 9, 10, 11).

This blue shift demonstrates mixing of eigenfunctions; therefore, the ν_8-mode should become infra-red active too, and show up at a frequency value of about 934 cm^{-1}, though significantly weaker than the blue shifted ν_8-peak. Accurate measurements using a two-laser-modulation technique clearly reveal this feature (see fig. 3 and ref. 27).

But there is more to C_2H_4; from the transition strength measurements of ref. 8, for $(C_2H_4)_2$ and $(C_2D_4)_2$, and from the sum-rule applied to the loosely bound dimer constituents, one can directly deduce that the out-of-plane ν_7-transition dipole moments are parallel, whereas those of the in-plane ν_{12}-transition are perpendicular to each other. According to theoretical chemists the two flat dimer constituents are shifted in their planes, with respect to each other, to minimize the interaction energy (ref. 30). Consequently, one expects two non-equivalent constituents, for what concerns the mutual perturbation of symmetry. In fig. 3 one finds some evidence of a doubling of the strong blue and the weaker red peak of the $(C_2H_4)_2$-complex, in agreement with this argument of non-equivalent constituents (ref. 28).
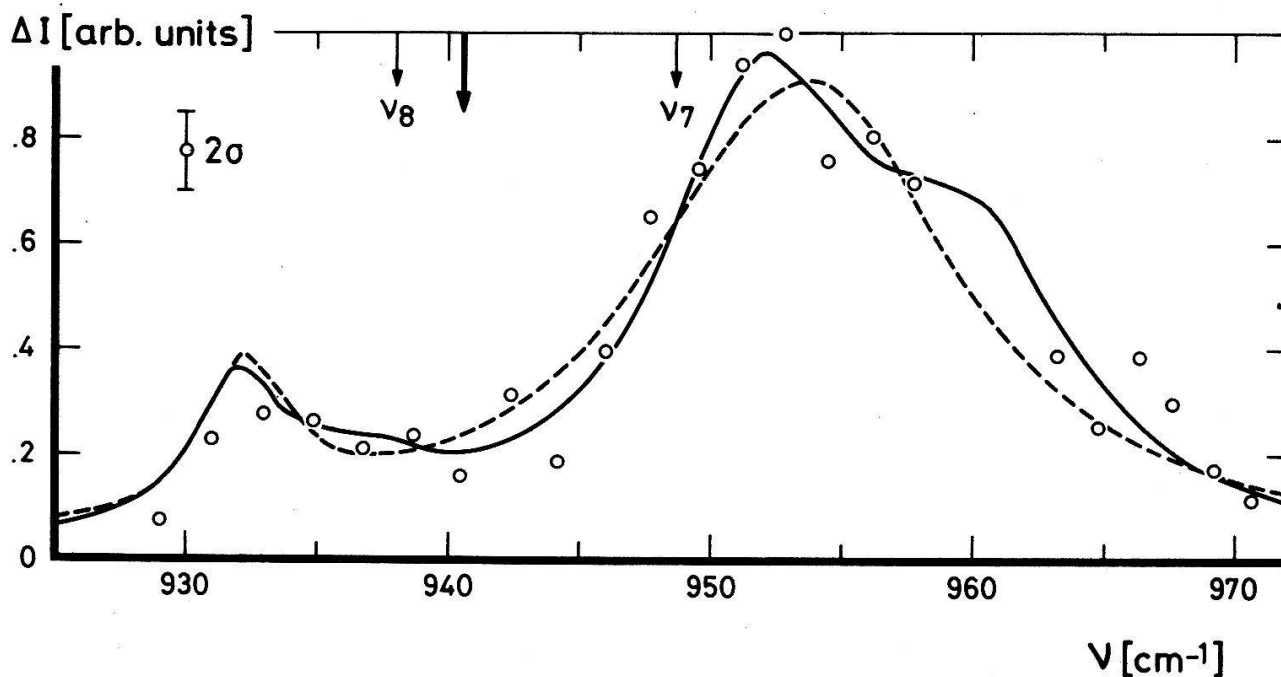
Figure 3

The $(C_2H_4)_2$ pre-dissociation spectrum, obtained by two-laser-modulation tech-
nique. The heavy arrow indicates the frequency at which laser 1 modulates the
$C_3H_5^+$-ion signal (10% modulation depth). Laser 2 scans in an on-off mode the
full spectrum; it produces a decrease in modulation depth which is displayed
as ΔI (1.0 arbitrary unit corresponds to a 0.7% decrease in modulation depth).
The i.r.-active ν_7-mode and the Raman-active ν_8-mode are indicated by light
arrows as measured for the monomer. Due to dimer-interaction the ν_8-mode
becomes partially i.r.-active and red shifted (Fermi-resonance). By the same
amount the ν_7-mode has been found blue shifted. Shown as a broken line is a
fit of the spectrum invoking two lorentzians centered at $\nu_8' = 932.5$ cm^{-1} and
$\nu_7' = 953.5$ cm^{-1} with fwhm $\Gamma_8' = 4$ cm^{-1} and $\Gamma_7' = 15$ cm^{-1}. A four centered
lorentzian fit (the solid line) was tried too, yielding $\nu_8' = 932.2$ cm^{-1},
$\nu_8'' = 937.2$ cm^{-1}, $\nu_7' = 959.1$ cm^{-1}, $\nu_7'' = 951.9$ cm^{-1}, $\Gamma_8' = \Gamma_8'' = 4.5$ cm^{-1} and
$\Gamma_7' = \Gamma_7'' = 9.4$ cm^{-1}.

8. Results and discussion; other unresolved i.r. pre-dissociation spectra

In the three lower rows of table 1, three cases are listed where the presence of the dimer perturbs and diminishes the effects of a Fermi-resonance which already manifest themselves strongly in the monomer. In all cases one deals with linear triatomic constituents which are excited into states with Σ^+-symmetry. Still there exists a relevant difference; whereas $(CO_2)_2$ and $(OCS)_2$ are known to arrange themselves in a staggered parallel configuration (ref. 31, 32, 33 and 34), the T-structure seems more probable for $(N_2O)_2$, due to the larger permanent dipole moments of its constituents (ref. 35). In accordance with these models, single broad lines have been found for the pre-dissociation spectrum of $(CO_2)_2$ and $(OCS)_2$ (ref. 8, 36), whereas the already mentioned doubly peaked structure is observed for $(N_2O)_2$ (ref. 17). Similar to the $(C_2H_4)_2$ case we suggest that the molecular vibration in the N_2O-constituents are perturbed differently by the dimer partners, yielding different diminuition of the Fermi-resonance effect. (For the parallel staggered configuration of $(CO_2)_2$ and $(OCS)_2$ this argument does not apply). That both peaks have different strength is attributed to the fact that in one case we deal with a //-transition, in the other with a ⊥-transition, with respect to the axis of the symmetric top as which $(NO_2)_2$ is regarded.

Cluster spectroscopy is still in its infancy, but recent progress in understanding the dimer-spectra strengthens our conviction that these larger and more complicated complexes will be spectroscopically attacked and their properties understood as well.

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