Laser Chem. 1988, Vol. 8, pp. 275–281
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Hole Burning in the IR Predissociation Spectrum of SF_6-dimers

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(Received December 16, 1987)

Hole burning experiments with two CO_2 lasers have been performed to obtain insight in the predissociation mechanism of SF_6-dimers. For the well known double peak predissociation spectrum, always two correlated holes are observed. Strongly enhanced widths of the holes are found for dimers with higher internal energy.

KEY WORDS: Spectroscopy, dimers, SF_6, CO_2-laser, hole burning.

INTRODUCTION

The SF_6-dimer IR predissociation spectrum in the neighbourhood of the ν_3 vibrational mode of the SF_6 monomer has been studied in detail.[1–4] This spectrum consists of two peaks, one blue shifted and the other red shifted with respect to the monomer ν_3-absorption frequency (948.0 cm^{-1}), see Figure 2a. The shifts and also the relative intensities of the two peaks can be explained by means of a resonant dipole-dipole interaction.[2,3] The interacting dipoles are the transition dipole moments of the two SF_6 monomers in the dimer. According to this model the red shifted peak corresponds to two in-phase transition dipole moments parallel to the dimer axis, whereas the blue shifted peak is due to in-phase transition dipole moments perpendicular to the

dimer axis. Recently the above mentioned model has been refined by including induction effects into the interaction hamiltonian.[5]

The model discussed up to this point produces a stick spectrum. To account for the experimental width of the two lines in the dimer spectrum, an extension has been proposed in which is assumed that a dimer consists of two free rotating molecules in the vibrational groundstate with rotational quantum numbers J_1 and J_2, respectively.[4] The groundstate of the dimer is given by $|\, v = 0, J_1 > |\, v = 0, J_2 >$. Only transitions with ΔJ_1, $\Delta J_2 = 0, -1$ or $+1$ can occur. According to this extension of the dipole-dipole interaction model each of the two dimer peaks consists of a *P*-, a *Q*- and a *R*-branch. The low frequency side, the centre and the high frequency side of the two observed peaks are respectively due to $\Delta J = -1$, $\Delta J = 0$ and $\Delta J = +1$ transitions in one of the monomers forming the dimer. In this case J stands for J_1, or J_2. As a further refinement the end over end rotation of the dimer is considered, which gives an extra broadening of the peaks.

The present work describes a two-laser experiment which gives insight in the origin of the width of the two peaks in the dimer predissociation spectrum. The new experimental results cannot be reconciled with the assumptions of the extended model.[4]

EXPERIMENTAL

The measurements have been performed using the molecular beam apparatus described in detail elsewhere.[4] The molecular beam is detected by means of a bolometer that monitors its energy content. Irradiation with CO_2-laser photons leads to dissociation of dimers. The fragments leave the molecular beam, yielding a diminution of the energy content of the beam and hence a change in bolometer signal. For a schematic picture of the apparatus see Figure 1.

Both the pump and the probe laser are cw CO_2-lasers. The probe laser, with fixed frequency and power, is modulated with a mechanical chopper. The dissociation due to this laser is measured by means of phase-sensitive detection of the bolometer signal. The pump laser, which is not modulated and constant in power, is tuned from laser-line to laser-line. Irradiation by the pump laser, on a frequency which leads to dissociation of dimers which contribute to the probe laser dissociation signal, yields a reduction of this signal. Thus, if pump and probe

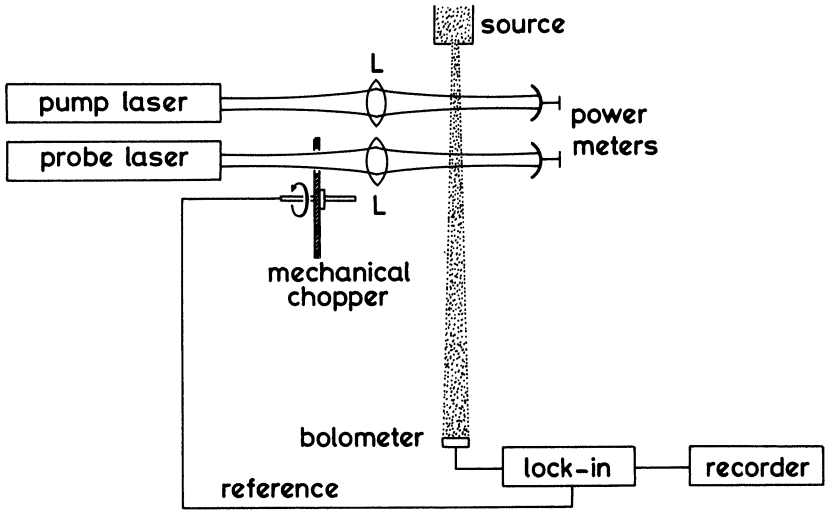

Figure 1 Schematic picture of the apparatus. The lens of the pump laser (probe laser) has a focal length of 37.5 cm (75 cm), resulting in a spot diameter of 0.6 mm (1.2 mm). For both lasers there is a more than complete overlap with the molecular beam. The bolometer, which consists of a 1×1 mm^2 doped Ge detector on a 2×5 mm^2 substrate of sapphire (Infrared laboratories), is operated at 4.2K. The N.E.P. at this temperature is 8.10^{-14} WHz$^{-1/2}$, the responsitivity is 5.10^4 V/W and the response time is 2.5 ms. The distance nozzle bolometer is about 50 cm.

laser excite dimers in the same initial state, pumping leads to a reduction of the probe laser dissociation signal. The attenuation of the probe laser dissociation signal is measured as a function of pump laser frequency.

The distance between the intersection points of the two lasers with the molecular beam is 7.5 cm. The measurements have been performed with a 1% SF_6 in helium mixture. The stagnation pressure P_0 was 5 atm. and the source temperature T_0 was 293K. The nozzle consisted of a platinum iridium electron microscope diaphragm (Siemens) with a diameter of 30 μm.

RESULTS

The experimental results are presented in Figure 2 and Figure 3. Figure 2a shows the one-laser dissociation spectrum as it has been

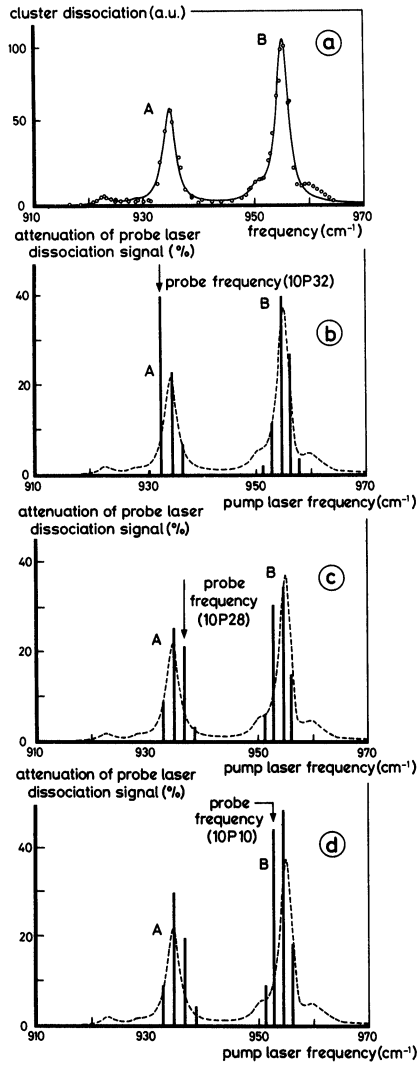

Figure 2 Figure 2a shows the dissociation spectrum of SF_6-dimers, as it was measured by Snels *et al.*[4] The Figures 2b, 2c and 2d show the results of the two laser experiments. The probe laser frequencies for 2b, 2c and 2d are respectively: 932.96 cm^{-1}, 936.80 cm^{-1}, and 952.88 cm^{-1}. The indications for the probe frequencies in the figures refer to the used CO_2 laser lines. The pump laser fluence (intensity) is always 0.4 mJ/cm^2 (1 kW/cm^2). For the Figures 2b and 2c the probe laser fluence is 0.4 mJ/cm^2, for 2d this fluence is 0.1 mJ/cm^2. The dashed lines in 2b, 2c and 2d indicate the one laser predissociation spectrum.[4]

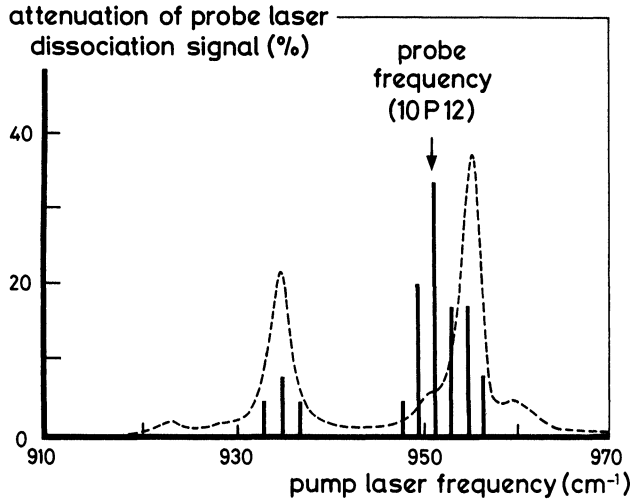

Figure 3 Results of a two laser experiment in which the probe laser irradiates at a transition frequency of the $^{34}SF_6$—$^{32}SF_6$-dimer. The picture shows that at this frequency there is also dissociation of $(^{32}SF_6)_2$. This is explained by the fact that the homogeneous lineshapes of these dimers have a tail at the probe frequency (951.20 cm^{-1}, the 10P12 CO_2-laser transition). The pump laser fluence is 0.4 mJ/cm^2, the probe laser fluence is 0.1 mJ/cm^2.

measured by Snels *et al.*[4]. The two main peaks (*A* and *B*) are assigned to the dimer $^{32}SF_6$—$^{32}SF_6$. The bumps around 950 cm^{-1} and 960 cm^{-1} are respectively due to $^{32}SF_6$—$^{34}SF_6$ and $(SF_6)_3$.

Figure 2b demonstrates that the dimer peak around 934.4 cm^{-1} (peak A) is inhomogeneous: The probe laser dissociation signal on the red wing of this peak is much more reduced by pumping at the red side of the peak than by pumping at the blue side. In addition, this figure shows that the red wing of peak A is correlated with the blue wing of peak B.

The Figures 2c and 2d show that the blue side of peak A is correlated to the red side of peak B. Comparison of Figure 2b with Figure 2c shows that the red wing of peak A is more inhomogeneous than the blue wing of this peak and the red wing of the other peak.

High resolution measurements with a CO_2-waveguide laser have been performed to look for narrow lines on top of the broad spectral structures. (Such lines with a width of 3.5 MHz have been found for C_2H_4-dimers.[6–8]) No narrow structures were observed for SF_6-dimers.

DISCUSSION

The inhomogeneity of the SF_6-dimer spectrum demonstrates that the coupling of excited states to the continuum of dissociated states is weaker than suggested by the width of the two peaks. For the red wing of peak A we find a width smaller than about 1 cm^{-1}, corresponding to a minimum lifetime longer than 5 ps. For the blue wing of the peak we find a significantly larger width of about 3 cm^{-1}, corresponding to a minimum lifetime of 1.5 ps.

According to the extension of the dipole-dipole interaction model of Snels and Fantoni,[4] as described briefly in the introduction, the red wings of the two peaks consist of *P*-transitions, whereas the blue wings consist of *R*-transitions. This means that for all four wings the transitions should originate from the same initial levels. As a result pumping on a blue wing should have the same effect on the probe laser dissociation signal as pumping on the corresponding red wing. The Figures 2b and 2c clearly demonstrate that our observations are not in agreement with the above mentioned consequences of the extended model. The Figures 2c and 2d show that the blue wing of peak A is more correlated with the red wing of peak B than with the blue wing of peak B, again in contradiction with the extended model.

According to the stick-model of Geraedts *et al.*[2,3] peak A (peak B) is situated $2\lambda(\lambda)$ to the red (blue) of the ν_3 monomer transition (948.0 cm^{-1}), with $\lambda = 6.8$ cm^{-1}. λ is given by:

$$\lambda = (\mu_{01})^2(4\pi\varepsilon_0)^{-1}\left\langle\frac{1}{R^3}\right\rangle,$$

in which μ_{01} is the transition dipole moment for a ν_3- transition in a SF_6 monomer and R is the distance between the monomers in the dimer. The brackets around $1/R^3$ indicate the average value of this quantity for a certain dimer state. From our measurements we conclude that not all the dimers have the same average intermolecular distance. Dimers with a relatively big average distance, and hence a small λ, are related to the blue wing of peak A and to the red wing of peak B, a correlation observed in the measurements shown in Figure 2c and Figure 2d. A bigger average distance stems from a higher internal energy, supposedly yielding a stronger coupling to the continuum after vibrational excitation. The dimers of high internal energy display a larger width (about 3 cm^{-1}, see Figures 2c and 2d) than those of low internal energy

(about 1 cm^{-1}, see Figure 2b), in agreement with the expectation. Further measurements are in progress.

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