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Improved Separation of the Rare Sulfur Isotopes by Infrared Multiphoton Dissociation of SF_6

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Abstract. The dissociation probabilities of $^{32}SF_6$ and some of $^{34}SF_6$ have been measured at a large number of CO_2 laser lines both at room temperature and at 140 K. The long-wavelength wing of this dissociation spectrum is exponential in the wavenumber. Its logarithmic slope is proportional to the inverse temperature. Selectivities are high enough at 140 K, that the photons are consumed only for the rare isotope in the case of $^{34}SF_6$ and nearly so for $^{36}SF_6$. For $^{33}SF_6$ further improvement of the selectivity would be desirable.

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A potential advantage of laser isotope separation is that the energy must not be spent for all the molecules or atoms, but is consumed only by the desired rare isotope. To attain this goal, the selectivities (ratio of probabilities) for absorption S_a and for dissociation S_d (molecular approach) must be larger than the inverse abundance:

$$S_a > x^{-1}, \quad (1)$$

$$S_d > x^{-1}. \quad (2)$$

Table 1. Abundances x_i of sulfur isotopes i

i	32	33	34	36
x_i [%]	95.0	0.76	4.22	0.014

For abundances of sulfur, see Table 1. In multiphoton dissociation S_d can be larger than S_a. The two conditions have been fulfilled so far only for separation of ^{13}C [1] and of D [2]. For the rare isotopes of sulfur they were not fulfilled so far, although SF_6 is the molecule most studied in infrared multiphoton dissociation. In [3] this was ascribed to special features of the SF_6 spectroscopy. Therefore it has been suggested [4] to isolate the rare isotopes by depletion of the most abundant one, ^{32}S. In fact the previous separations of macroscopic quantities of sulfur [5–7] employed just this method. Best published selectivities for the rare isotopes were $S_d = 3$ for $^{34}SF_6$ at room temperature [8] and $S_d = 5$ for $^{33}SF_6$ at 170–190 K [9].

We measured the dissociation probability of $^{32}SF_6$ over a wide range of CO_2 laser frequencies, and over a smaller range also $^{34}SF_6$, both at room temperature and at 140 K. We used an energy density of $\phi = 5$ J/cm^2 throughout, which yields dissociation probabilities P_d of up to 20%. Reduced ϕ could give better selectivities, but only on expense of seriously reduced P_d and of reduced quantum yield. Especially at the lower temperature S_d was found for $^{34}SF_6$ well within condition 2 and not far from it for $^{36}SF_6$. Even for $^{33}SF_6$ it would now be more economic to dissociate directly this isotope instead of depleting the most abundant one, although condition 2 is not met.

The origin of the long-wavelength wing of the dissociation spectrum and its temperature dependence is also discussed. Probably they are both caused by the near-resonance enhancement of direct multiphoton transitions.

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1. Experimental

The experimental setup is shown in Fig. 1. It consists of a pulsed line-tunable CO_2 laser, a waveguide cell in which a sample of gaseous SF_6 is irradiated and dissociated and a cw CO_2 laser whose transmission through the waveguide is monitored before and after irradiating the SF_6 sample. From this change of transmission the dissociation yield was deduced.

The pulsed CO_2 laser is a modified EMG 200 laser from Lambda-Physik. It is operated with a gas mixture of $CO_2:N_2:He = 30:10:60$ at a total pressure of 340 mbar. The resonator consists of a concave grating of 10 m radius of curvature and with 150 lines/mm, and a germanium etalon as output coupler. The maximum reflection of this etaton is 78% and, as its free spectral range (0.62 cm^{-1}) can be passed through by a temperature change of 5 K, it is kept at a constant temperature. In order to get a diffraction limited beam, an aperture with a diameter of 10 mm is inserted in the cavity, as the mode quality is important for a good coupling and transmission of the laser radiation into the waveguide. The maximum pulse energy delivered by this laser is about 250 mJ, on the line 10P40, the half-height pulse duration being approximately 100 ns.

The waveguide is a one meter long stainless steel tube of 1.8 mm inner diameter. This dimension was selected in order to attain in the waveguide an energy density well above the dissociation threshold with the available energy of the pulsed laser.

In order to get the highest transmission it is important to have no angle between the incoming beam and the waveguide axis. Moreover, two conditions must be fulfilled [10]:

1) the laser beam must have its waist, w_0, at the entrance of the waveguide and

2) $w_0 = 0.5$ a to 0.65 a, where a is the radius of the waveguide. For this reason a KCl lens of about 70 cm focal length is used to couple the laser radiation into the waveguide. Under these conditions, about 70% of the incident energy was transmitted.

In order to avoid any bending of the tube, that would be detrimental to the transmission, the waveguide is mounted on a rigid support. Metal bars, connected to this structure and dipped into liquid N_2, make it possible to cool the waveguide. Two thermocouples provide temperature monitoring and feedback to a control circuit for counterheating by means of power resistors mounted onto the structure. In this way it is possible to adjust the temperature of the waveguide down to 100 K and to keep it constant.

The windows and the valves for the gas supply are mounted as close as possible to the ends of the tube to have the smallest non-irradiated volume. In the present configuration the relation of volume in the waveguide to the volume in the ends is about 1:1.

The probe laser is a line tunable cw CO_2 laser (Spectra Physics) equipped with a piezoelectric control of the cavity length that allows a fine tuning of the emission frequency over about 30 MHz of the laser gain profile. It has an output of about 10 W in a TEM_{00} mode quality. A stable transverse mode is required for a constant transmission of the waveguide.

The long-term amplitude stability is within 5% while the frequency deviation can be kept less than 5 MHz with the help of an auxiliary cooling unit capable of keeping the laser tube at a constant temperature (10.5 °C) within 0.1 °C. The frequency stability is required because of the small Doppler width (10 MHz at room temperature) of SF_6. Before reaching the waveguide, the cw beam passes through a chopper (duty cycle 1:1) operating at a frequency of 50 Hz and a series of attenuators, so that the power density at the entrance of the waveguide is about 10 mW/cm^2. This small intensity is required for avoiding any saturation effect. In fact we found that at room temperature 0.1 mbar SF_6 begins to be bleached more and more above 50 mW/cm^2 of the 10P12 radiation.

D_1 and D_2 are HgCdTe infrared detectors cooled by liquid nitrogen, both used with lock-in amplifiers. The ratio between their signals determines the transmission of the SF_6 gas sample. The value of the ratio (D_2/D_1) as well as the signal from the first detector are then displayed on a digital voltmeter and recorded on a plotter. The steady-state conditions are achieved a few hours after the probing system has been switched on. In this case the stability of the signals is well within 2%.

We employed 10P12 and 10P36 for monitoring ^{32}S and ^{34}S, respectively. Figure 2 shows their position as well as the associated experimental absorption cross-

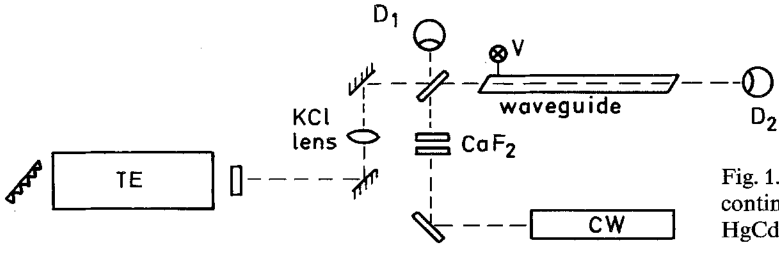

Fig. 1. Experimental setup. (TE: pulsed CO_2 laser, CW: continuous wave CO_2 probe laser, CaF_2: attenuators, D_1, D_2: HgCdTe detectors, V: vacuum and gas supply)

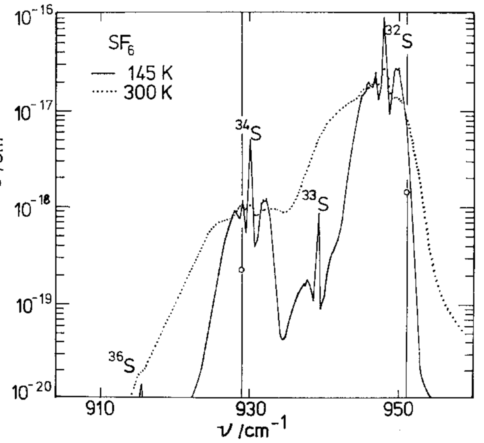

Fig. 2. IR absorption spectra at 145 K (simulated [11]) and at room temperature (measured). Vertical lines and points show the two probe laser frequencies with the absorption cross-sections measured at 140 K

sections together with a simulated linear absorption spectrum of SF_6 at 145 K [11]. The cross-section especially at 10P36 is lower than the simulated spectrum, presumably because this laser line falls between two rotational lines of SF_6.

The dissociation probability P_d is calculated according to the relation

$$P_d = [1-(n/n_0)^{1/N}]f, \tag{3}$$

where n and n_0 are respectively the SF_6 concentration before and after the irradiation, N is the number of irradiating pulses and $f(\sim 2)$ is the ratio between the total volume and the irradiated volume. This fill factor takes account of the diffusion from nonirradiated parts of the cell into the waveguide in the time between the pulses.

2. Results

Figure 3 shows a dissociation spectrum of $^{32}SF_6$ obtained at 300 and 140 K, respectively.

In order to ensure collisionless regime, the SF_6 pressure was kept low (0.05 and 0.03 mbar for room and low temperature, respectively). The energy density within the waveguide was about 5 J/cm². The number of laser shots for each different excitation frequency was chosen so that the resulting dissociation was no more than 50%.

The dissociation curve for $^{34}SF_6$ (dashed line in Fig. 3) was obtained by a parallel displacement of the curve for $^{32}SF_6$ equal to the isotopic shift (17.4 cm⁻¹ [12]) in the ν_3 vibration.

In order to verify this procedure, a part of the dissociation spectrum for $^{34}SF_6$ around the expected maximum was measured (asterisks in Fig. 3). As can be seen, the wavenumber of maximum dissociation is confirmed. Note however, that the absolute values of the dissociation probability are quite a bit lower. This is probably due to the increased SF_6 pressure (0.3 mbar), which was chosen to obtain a good sensitivity also for $^{34}SF_6$.

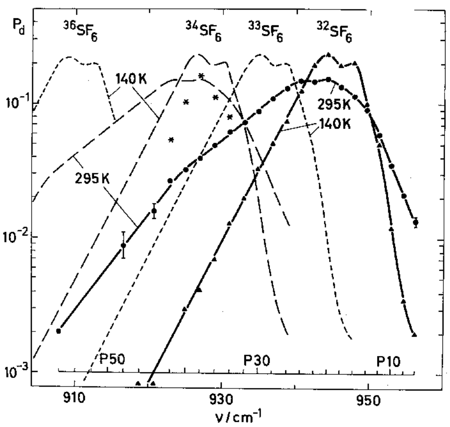

Fig. 3. Dissociation probabilities P_d of the four SF_6 isotopes. Dots and asterisks are experimental. The curves for the three heavy S isotopes are derived from the dissociation spectra of $^{32}SF_6$, displaced by the isotope shifts

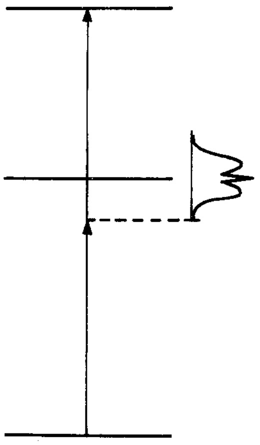

Fig. 4. Near-resonance enhancement of a direct two-photon transition. Near the one-photon energy the (one-photon) spectrum of the ground state (Fig. 2) is shown schematically

3. Discussion

3.1. The Origin of the Long-Wavelength Wing

From the early times of multiphoton dissociation there has been agreement, that the first few excitation steps determine the wavelength dependence and thus the selectivity. An early description [13] suggested subsequent P, Q, and R type transitions in the first three steps. This mechanism predicts [14] a wavelength dependence like the Q branch(es) of the $v=1\rightarrow 2$ transition. However experimental evidence [15–17] and quantum mechanical calculations [18–20] showed that (stepwise or especially the) direct two-photon resonances are far more important. Therefore it is tempting to assign the long-wavelength wing of the dissociation spectrum (Fig. 3) to higher ($n-th$) order direct multiphoton transitions. Their shift from the band origin of the infrared spectrum (948 cm^{-1}) would be $x(n-1)$; the effective anharmonic constant $x' \sim -2.8\ \mathrm{cm}^{-1}$ describes approximately the largest shifts of the ν_3 levels ([14], more accurate description in [21]). (The higher levels of this mode are split into multiplets.)

Each individual multiphoton transition will have a width, generated by rotational and hot band structure, which is not broader than the one-photon spectrum; sometimes it is even narrower because of rotational selection rules. But for each $n \geqq 2$ there are several n-photon resonances, because the $v_3 = n$ levels are split by anharmonicity. The envelope of all these transitions can extend to far longer wavelengths than the one-photon spectrum. The roughly exponential dependence on wavenumber (or on n) appears also plausible, although this shape deserves more theoretical attention. Such an exponential shape implies an asymptotically constant selectivity for long wavelengths (see the case of ^{33}S in Fig. 5 below).

But if the long-wavelength tail is caused by multiphoton transitions (most of which start from the vibrational ground state), what causes its temperature dependence? If each individual of these transitions broadens just like the one-photon spectrum, the total width cannot broaden more. Typically it will even be less. According to Fig. 3 the long wavelength wing of the dissociation spectrum shifts by 12 cm^{-1} at 10% height, whereas the ir spectrum shifts by only 6 cm^{-1} (Fig. 2). (This latter broadening is mainly caused by rotation. Hot bands contribute little, according to their anharmonic shifts [12].)

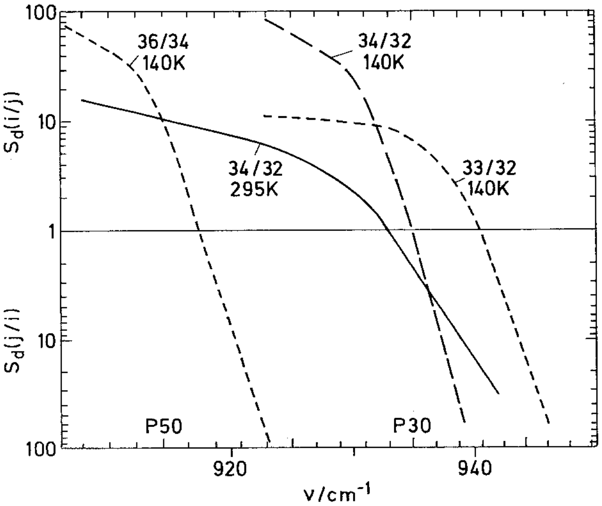

Fig. 5. Dissociation selectivities $S_d(i/j) = P_d(i)/P_d(j)$, at room temperature and 140 K, calculated from the curves of Fig. 3

We suggest that the temperature dependence of dissociation is caused by the enhancement of the multiphoton excitations by nearly resonant intermediate transitions. The detuning of the latter from the laser frequency depends on their initial rotational and vibrational states and therefore on temperature, and this detuning governs the transition probabilities. This mechanism is illustrated in Fig. 4 by the example of a direct two-photon excitation. Its transition probability α_2 depends on the detuning $\nu_J - \nu_l$ of the one-photon transitions from the laser frequency ν_l; the rotational component ν_J has a distance from the band origin ν_0 of the 0→1 transition of

$$\nu_0 - \nu_J \sim 2BJ \tag{4}$$

(P branch). B is the effective rotational constant ($\sim 0.09\ \mathrm{cm}^{-1}$) and J is the quantum number of the initial rotational state. The population of the latter (Boltzmann factor) is

$$b_J = (2J+1)^2 \exp[-BJ(J+1)hc/kT](B/kT)^{3/2} \tag{5}$$

$$\sim (\nu_0 - \nu_J)^2 \exp[-(\nu_0 - \nu_J)^2 hc/4BkT] \times B^{-1/2}(kT)^{-3/2}\,. \tag{6}$$

The dependence of α_2 on the detuning can be written as a Lorentzian

$$\alpha_2 \propto [1 + (\nu_l - \nu_J)^2/W^2]^{-1}\,, \tag{7}$$

where W characterizes the transition probability in the wings and contains the laser intensity besides molecular parameters; a more common relation (for large detunings) is

$$\alpha_2 \propto W^2/(\nu_l - \nu_J)^2 \tag{8}$$

which is usually derived by means of perturbation theory [23]. Equation (7) differs from (8) by the 1 in the denominator. It has been added to prevent divergence of α_2 for small detunings.

Instead of considering individual rotational components, it is better to integrate over some spectral bandwidth (to decrease resolution), because there will be strong overlap of the various vibrational multiplet components of the multiphoton transitions of different order. The two-photon $\Delta J = 0$ band strength $\int \alpha_2 b_J d\nu_J$ can be derived from (6–7) by somewhat lengthy calculation to contain an exponential:

$$\int \alpha_2 b_J d\nu_J \propto \exp[-(\nu_l - \nu_0)^2/4BkT]\,, \tag{9}$$

if $W \ll \nu_l - \nu_0$. For large W, the wavenumber dependence disappears, just like for saturation. Similar consideratons probably also apply for higher order multiphoton transitions. If instead of (4) a square dependence

$$\nu_0 - \nu_J \sim (B'' - B')J(J+1) \tag{4a}$$

dominates, then a simple exponential replaces the Gaussian in (9), and this exponential also survives the integration:

$$\int \alpha_2 b_J d\nu_J \propto \exp[(\nu_0 - \nu_l)hcB/\Delta BkT] . \qquad (9a)$$

Equation (4a) applies to the far wing of a P branch as well as to a Q branch. The latter is the only allowed branch for the transition to the $\nu_3 = 2(A_{1g})$ state which as an intermediate resonance can enhance higher order multiphoton transitions. Analogous considerations for enhancement by successive hot bands instead of successive rotational components will probably result in a simple exponential like (9a).

Lowering the temperature increases the dissociation in the center of the spectrum and decreases it in the short wavelength wing. This is just as observed also in the infrared spectrum, where it is due to the change of population in the corresponding rotational states. But will the first absorption step be the bottleneck of excitation at short wavelengths and will it thus determine the dissociation spectrum in this range? A closer inspection of the level scheme in [14] shows that three subsequent R branch transitions at short wavelengths (and Q branch transitions at 948 cm^{-1}) to the $v_3 = 3$ (A_{2u}) state nearly coincide. The next absorption step would certainly be a bottleneck, because its spectrum is shifted to longer wavelengths. The dissociation spectrum should therefore also be shifted to longer wavelengths. This is in contrast to observation. If however the laser stimulates a P branch emission from $v_3 = 3$ to another sublevel of $v_3 = 2$, then absorption returns into resonance for several steps. So there would be no bottleneck after the third absorption step. In this case, *in fact*, the dissociation should follow the R branch of the first or first three absorption steps, as observed. This is another evidence for the importance of intermediate emission steps, as discussed in [14].

The importance of absorption selectivity was pointed out in the introduction. So the absorption of $^{32}\mathrm{SF}_6$ especially at long wavelengths would be interesting. Since the dissociation can change drastically, even if the mean absorbed energy changes only little, it is conceivable, that the absorption spectrum is much flatter than the dissociation spectrum and that S_a is much smaller than S_d. On the other hand, if the rate determining excitation step is the very first step ("early bottleneck") as in the mechanism suggested above (for long wavelengths only), the absorbed quanta and the dissociation yield tend to be proportional to each other. The two spectra then have the same shape, and quantum yields do not depend on wavenumber.

Absorption spectra in cold (probably around 30 K) molecular beams are in fact fairly narrow [24–27]. Unfortunately they do not cover our wavelengths, temperatures and energy densities. Published spectra at room temperature are much flatter [14]. But they are probably distorted by the presence of collisions [28].

3.2. *Selectivity and Isotope Separation*

Figure 5 shows selectivities calculated from the dissociation spectra of Fig. 3

$$S_d(i/j) = P_d^i / P_d^j \qquad (i, j = 32, 33, 34, 36) .$$

Since only few experimental data of P_d^{34} and none of the other rare isotopes are available, we took the shifted curves of Fig. 3 for this calculation. The actual selectivities will be slightly smaller.

In order to spend the photons primarily for $^{34}\mathrm{SF}_6$ while separating $^{34}\mathrm{S}$, the selectivities S_a and S_d should be >23 according to (1, 2). At room temperature S_d nearly attains this value at the laser line $P56$. This appears already very attractive for separation of $^{34}\mathrm{S}$, in particular because cooling is not necessary. But the process depends critically on the absorption probabilities of the two isotopes at $P56$. They are not known so far.

At 140 K S_d is much better (50...90) even near the maximum of dissociation probability of $^{34}\mathrm{SF}_6$. If S_a is not *much* worse there, most photons will be consumed only for $^{34}\mathrm{SF}_6$.

This goal is more difficult to attain for $^{36}\mathrm{S}$ because of its low abundance. Selectivities of S(36/34) $>300 (= x_{34}/x_{36})$ and S(36/32) > 7000 would be desirable for S_d and S_a. At 140 K only $S_d(36/34) \sim 70$ is attained at the most favorable laser line $P56$. Extrapolation to lower temperatures T is however possible, since the logarithmic slopes of P_d (Fig. 4) seem to be $\propto T^{-1}$. The desired dissociation selectivities would be attained between 110 and 120 K. On the other hand, at this temperature the vapor pressure is only 0.08 mbar, so that the density of $^{36}\mathrm{SF}_6$ would be 7×10^{11} cm^{-3} only. With an absorption cross-section around 10^{-19} cm^2 [14] the absorption length would be 150 km. Assuming that a 1 km setup is realistic, only 1% of the photons would be absorbed. Then it would be more favorable, to select a 15 times higher pressure (at 140 K the vapor pressure is 1 mbar), at which 10% would be absorbed by $^{36}\mathrm{SF}_6$ and 90% by the other isotopes.

The selectivity for $^{33}\mathrm{S}$ (7 to 10) is far from ideal (>130). The quanta absorbed by this isotope alone can be written as a product of absorption cross-section σ (at 5 J/cm^2), the number density n and the photons per cm^2 ϕ

$$Q_{\mathrm{ideal}} = \sigma_{33} n_{33} \phi .$$

The total number of absorbed quanta Q_1 is about 20 times larger

$$Q_1/Q_{\mathrm{ideal}} = 1 + \sigma_{32}n_{32}/\sigma_{33}n_{33} + \ldots = 21\,,$$

where $S_a = \sigma_{33}/\sigma_{32} = 7$ has been assumed. The product will contain 5% ^{33}S. If it is chemically reconverted to SF_6 and the irradiation is repeated, again more photons than ideal ($Q_2/Q_{\mathrm{ideal}} = 3$) are consumed.

From this product (30% ^{33}S), after reprocessing, probably the $^{32}SF_6$ would be depleted, leaving arbitrarily pure $^{33}SF_6$. This third step consumes again a few photons ($Q_3/Q_{\mathrm{ideal}} \sim 2.3$), so that over all three steps 26.3 times the smallest conceivable number of photons is consumed per separated mole of ^{33}S. This is 5 times less than required for the depletion method ($Q_{\mathrm{depl}}/Q_{\mathrm{ideal}} = x_{33}^{-1} = 133$), in which the most abundant isotope $^{32}SF_6$ is dissociated instead of the desired one.

4. Conclusion

Provided that the absorption selectivity will not be *much* smaller than the dissociation selectivity, $^{34}SF_6$ can now be separated with the minimum number of photons required. At 140 K a product of 75% isotopic purity will be obtained in one step. The other 25% are light isotopes, mainly ^{32}S, which in a second step (after chemical reprocessing) can be easily removed with high selectivity even at room temperature.

Also ^{36}S can be highly enriched in a single step: to 20% or, if most of the $^{34}SF_6$ is removed before, even to 50%. Compared to the depletion method, several thousand times less photons (and SF_6) are consumed thereby. Note that the laser line *P*56, which is suitable for this enrichment, is fairly effective because of an accidental overlap with a sequence band line of the gain medium.

For $^{33}SF_6$ the situation is less favorable. Although, compared to the depletion method, a factor of 5 less photons is consumed in a three-step separation (which is required for high enrichment), another factor of 26 could be saved, if a process can be found with a selectivity much higher than 130. Two-wavelength exitation should be investigated for this purpose.

It would also be interesting how much the pressure can be increased, before the selectivity breaks down. Higher pressure would reduce the absorption length. This would be important especially for the rarest isotope (^{36}S), where this path would be longest.

In view of its importance for isotopic selectivity, the long-wavelength wing of the dissociation spectrum deserves further theoretical investigation. Will it be exponential also for other molecules? On which molecular parameters will its slope or its extension depend? Is the intensity important? Since this wing is probably governed by the first absorption step, will high order multiphoton resonances be observable by a tunable laser? It is surprising that after more than ten years of infrared multiphoton dissociation its wavelength dependence is not quantitatively understood, although it is governed by the first few steps.

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