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Infrared Multiple-Photon Absorption in Polyatomic Molecules: Silicon Tetrafluoride, Cyclobutanone, Ammonia, and Hexafluorobenzene†

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Abstract: Detailed absorption data in the fluence range 0.03–0.8 J/cm^2 for SiF_4 ($\bar{\nu}_{irr}$ = 1025.3 cm^{-1}, pressure range 0.4–50 torr) as well as less extensive data for C_4H_6O ($\bar{\nu}_{irr}$ = 1073.3 cm^{-1}, pressure range 1.4–6.0 torr) are presented. The data can be represented in terms of a simple differential law and reasons for so doing are discussed. The results are compared with similar data for NH_3 and C_6F_6. It is shown how these data can be conveniently manipulated to obtain absorption cross sections for molecules with average energy $\bar{E}$, $\sigma^{exptl}(\bar{E})$. These experimental cross sections are compared with model values, $\sigma_{net}(E)$, associated with "energy shell" E and reasons for the energy variation of $\sigma^{exptl}(\bar{E})$ considered. The consequences of this variation as well as other factors which affect the efficiency of reaction in both direct and sensitized laser chemistry are discussed.

It has become increasingly clear that infrared laser chemistry studies can benefit from concomitant photophysical measurements on energy absorption.[1-5] However in a real experiment the fluence (F) and the number of photons absorbed per molecule (n) can vary significantly along the cell path length (Figure 1). This can have important consequences in laser chemistry since not only the type but also the extent of reaction can vary markedly with n or E_{abs} (the energy absorbed per mole).[6-8] Thus the most readily determined quantities like $\bar{n}$, the number of photons absorbed per molecule averaged over the cell length, may not give a fully adequate account of the situation, where $\bar{n}$ is expressed in terms of the incident and transmitted fluences (F_0 and F_t), the molecular concentration (N_t), the cell path length (L), and the laser frequency (ν) by the equation

$$\bar{n} = \frac{(F_0 - F_t)}{L}\left(\frac{1}{h\nu}\right)\left(\frac{1}{N_t}\right)$$

What is required is $\bar{n}(P,F)$, the average number of photons absorbed when the pressure is P and the fluence is F. Since this equals $-(dF/dl)(1/h\nu)(1/N_t)$, one way in which the "optical depth problem" can be handled is to take raw integral data and determine the empirical differential law, i.e., the form of dF/dl, which best fits the results. This is the method employed in this paper. Data in such a form are also useful when experimental results are compared with modeling studies since the latter generally implicitly assume that all molecules are subject to the same fluence. It may be noted that because of the high powers involved $\bar{n}(P,F)$ is not expected to, and does not, follow the Lambert–Beer law.

Differential laws allow not only reconstruction of axial energy deposition profiles and comparison of data with theory but, as we shall see, can easily be manipulated into forms which give information about how absorption cross sections vary with excitation energy. In turn this suggests factors which are influential in deciding the effectiveness of a molecule as a harvester of energy from the laser radiation field.

This paper reports detailed absorption measurements on SiF_4 as well as less extensive measurements on C_4H_6O (cyclobutanone) and C_6F_6 (hexafluorobenzene).[9,10] The absorptive properties of these molecules together with those of NH_3, a molecule on which we have reported previously,[2] are compared. Factors which relate to the efficiency with which these molecules absorb energy from the laser field are discussed and their effectiveness as sensitizers[1c,11] in laser chemistry compared.

Experimental Section

Energy absorption measurements reported in this work for SiF_4 (Matheson) and C_4H_6O (Aldrich Chemical) were carried out with use of a split-beam monitoring system described in detail elsewhere.[1b] There were no modifications to the techniques reported by us previously.[2] Most frequently a 19 mm diameter aperture was used to select a central portion of the laser beam; this ensured a fairly uniform transverse intensity. Absorption cells, which varied in length from 0.48 to 121 cm, were either Pyrex or stainless steel equipped with polished KCl windows. All samples were carefully vacuum distilled and degassed on a conventional high-vacuum line before use.

Primary experimental measurements consisted of the determination of F_0, F_t, and F_{abs} under a variety of conditions (Figure 1). From plots of the type shown in Figure 2, the absorption parameters A_1, A_2, and B_1 in the differential form of the absorption law (eq 1) were determined by a least-squares procedure.[12] In terms of eq 1 (see below) we write

$$F_{abs} = \int_0^L \frac{A_1F + A_2F^2}{1 + B_1F}\,dl = f(A_1,A_2,B_1,L,F_0)$$

A_1, A_2, and B_1 are then found by minimizing the residual R with respect to A_1, A_2, and B_1 for a set of i experimental values where $R = \sum_i\{F_{abs}^{(i)} - f(A_1,A_2,B_1,L,F_0^{(i)})\}$. Details for determining $\partial f/\partial A_1$, $\partial f/\partial A_2$, $\partial f/\partial B_1$ may be found in the thesis of one of the authors (V.S.).[13]

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† This paper is dedicated to George S. Hammond on the occasion of his 60th birthday. Among his many contributions he drew the attention of photochemists to the importance of sensitization in organic photochemistry. Through his work he has influenced many including one of the authors of this paper (C.S.).

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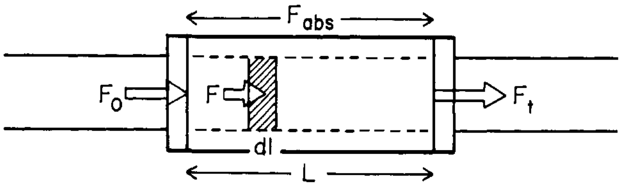

Figure 1. Integrated and differential absorption parameters, see text.

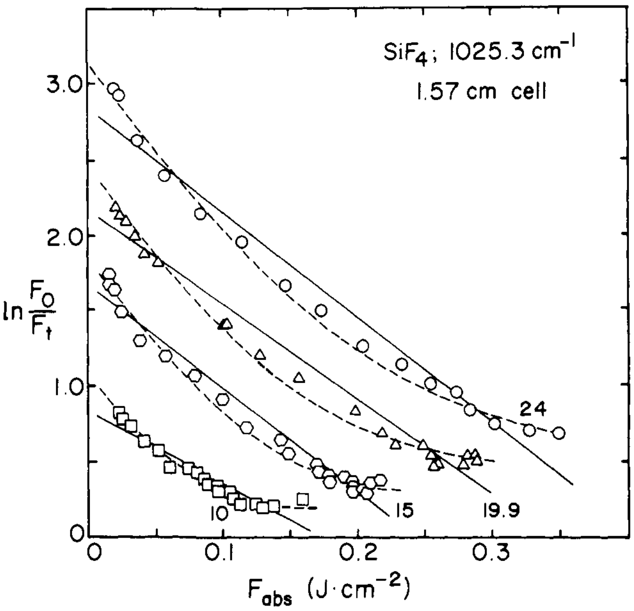

Figure 2. Absorbance as a function of absorbed fluence for various pressure of SiF_4 irradiated at 1025.3 cm^{-1}. Pressures in torr are indicated beside each set. Best straight line fit (—); fit obtained by integration of eq 1 (- - -).

The vibrational frequencies (cm^{-1}) used in computing the densities of states, the thermal vibrational energies (E_T), and the heat capacities (C_v) for the molecules studied are as follows. The numbers in brackets refer to the degeneracies.

NH_3:[14] 3337, 950, 3444 (2), 1627 (2)

SiF_4:[14] 800, 268 (2), 1032 (3), 389 (3)

C_4H_6O:[15] 2975, 2930, 1800, 1480, 1470, 1400, 955, 850, 670,
2975, 1200, 1000, 902, 2930, 1400, 1330, 1240, 1120,
850, 455, 3000, 3000, 1200, 1070, 730, 400, 50

C_6F_6:[16,17] 763, 1330, 645, 719, 248, 1252, 201, 645 (2), 137 (2),
1493, 556, 210, 365 (2), 1533 (2), 1019 (2), 313 (2),
1656 (2), 1162 (2), 440 (2), 267 (2)

Results and Discussion

1. Form of Empirical Absorption Law. In a previous publication on ammonia we showed[2] that the integral experimental absorption data could be represented in terms of an empirical differential equation

$$\bar{n}(P,F) = \frac{A_1(P)F + A_2(P)F^2}{1 + B_1(P)F}\left(\frac{1}{h\nu}\right)\left(\frac{1}{N_t}\right) \qquad (1)$$

where A_1, A_2, and B_1 are absorption parameters determined from the data as outlined above. They may be functions of pressure. Under low signal conditions, F→O, eq 1 degenerates to the Lambert–Beer law and integration yields $\ln (F_0/F_t) = A_1(P)L$ which for a given pressure and cell length (L) is a constant independent of F_0, F_t, or F_{abs} ($=F_0 - F_t$). Not surprisingly, the data in Figure 2 clearly show that this simple situation is not applicable to SiF_4 under our fluence conditions ($F > 0.03$ J/cm^2) and this is true for all the other molecules studied.

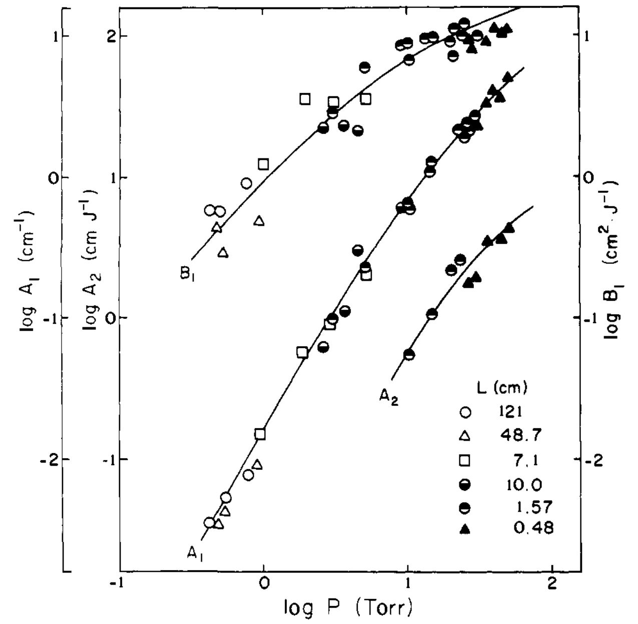

Figure 3. Absorption parameters for SiF_4 excited at 1025.3 cm^{-1}. The path lengths of the various cells used are shown in the inset.

At the next level of approximation in eq 1, $A_2 = 0$ and $B_1 \neq 0$, integration yields $\ln (F_0/F_t) = A_1(P)L - B_1(P)F_{abs}$. This equation predicts that at a given pressure $\ln (F_0/F_t)$ should be a linear function of F_{abs} with slope $-B_1(P)$. Although such an equation, which is of the type found for a saturative 2-level system,[18] is obeyed over a limited fluence range, the curvatures of the plots in Figure 2 indicate that need for the inclusion of at least one further term (A_2F^2) in eq 1.

Obviously data in the form of eq 1 can immediately be used to see how $\bar{n}$ varies with F at a given P or how $\bar{n}$ varies with P at a given F, both common ways of graphically presenting information.[2,19-21] Equation 1 can also be used for obtaining absorption cross section data. At a fluence F, the experimental differential cross section is given by

$$\sigma^{\text{exptl}}(F) = h\nu\ (\mathrm{d}\bar{n}/\mathrm{d}F) \qquad (2)$$

where the right-hand side is obtained by differentiation of eq 1. In section 3 we shall see how such cross sections can be related to cross sections associated with models for the excitation dynamics. For F→O, the experimental cross section is given by

$$\sigma_0^{\text{exptl}} = h\nu(\mathrm{d}\bar{n}/\mathrm{d}F)_{F\to O} = A_1(P)/N_t \qquad (2a)$$

This is the low-signal cross section where A_1 (cm^{-1}) can be identified with the low-signal absorption coefficient.

2. Absorption Data. (a) SiF_4 ($\bar{\nu}_{irr}$ = 1025.3 cm^{-1}). The absorption parameters A_1, A_2, and B_1 for a range of pressures and cell lengths are shown in Figure 3 for incident fluences from 0.03 to 0.8 J/cm^2. It is to be noted that one complete set of points at a given pressure in Figure 2 generates only a single set of $A_1(P)$, $A_2(P)$, and $B_1(P)$ so that Figure 3 summarizes a large amount of experimental data. The A_2 values do not encompass the same range as the A_1 or B_1 parameters because at lower pressures the

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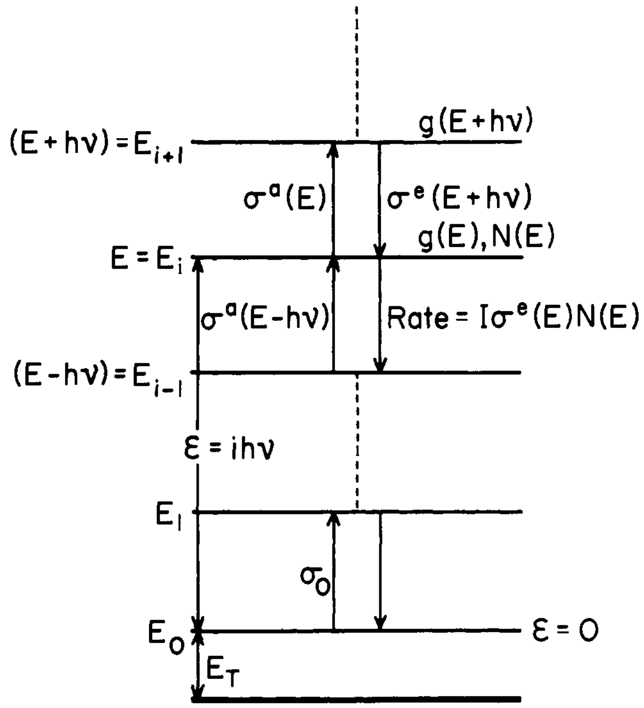

Figure 4. Schematic of energy absorption model. See text for definition of terms.

ln (F_0/F_t) vs. F_{abs} plots are sufficiently compressed to make curvature determination difficult (see Figure 2). In section 4 we shall return to a discussion of the low-signal cross sections, σ_0^{exptl}, which can be derived from the A_1 parameters.

(b) NH_3 ($\bar{\nu}_{irr}$ = 1076.0 cm^{-1}), C_4H_6O ($\bar{\nu}_{irr}$ = 1073.3 cm^{-1}), and C_6F_6 ($\bar{\nu}_{irr}$ = 1023.2 cm^{-1}). Experimental data for NH_3 have already been reported.[2] Less extensive studies were carried out on C_4H_6O. For this molecule σ_0^{exptl} was independent of pressure over the range 1.4–6 torr and had a value of $(2.0 \pm 0.2) \times 10^{-19}$ cm^2. Typical sets of absorption parameters were $A_1 = 0.013$ cm^{-1}, $A_2 = 0.004$ cm/J, and $B_1 = 2.1$ cm^2/J at 2.0 torr, while at 6.0 torr the corresponding values were 0.04 cm^{-1}, 0.017 cm/J, and 1.8 cm^2/J. For C_6F_6[9] σ_0^{exptl} was also pressure independent over the range 0.3–7.1 torr with a value of $(1.6 \pm 0.2) \times 10^{-18}$ cm^2. At 7.1 torr the absorption parameters had values $A_1 = 0.33$ cm^{-1}, $A_2 = 0.35$ cm/J, and $B_1 = 3.7$ cm^2/J. These data will be used in the following discussion.

3. Energy Dependence of Absorption Cross Sections. It has become a widespread practice to discuss both energy absorption from the laser field and the resulting chemistry induced by the multiple photon excitation (MPE) in terms of a coarse-grained master-equation approach.[22-26] It is therefore convenient to cast the experimental data in a format which facilitates comparison with this viewpoint. This will also yield insight into the gross factors which may influence the efficiency with which molecules "harvest" energy from the radiation field. The familiar radiation stepladder is shown in Figure 4. The total vibrational energy E associated with an "energy shell" is given by $E = \epsilon + E_T$ where ϵ is the energy of the i photons absorbed and E_T is the thermal vibrational energy possessed before excitation. The superscripts a and e ascribed to the cross sections σ refer to induced absorption and emission, respectively. $g(E)$ is the density of states associated with shell with energy E, where the concentration of molecules is $N(E)$. As assumed by most workers,[22-24] and as can be readily derived, we take $\sigma^a(E)/\sigma^e(E + h\nu) = g(E + h\nu)/g(E)$. It was also suggested that the absorption cross sections had an energy dependence of the form[23] $\sigma^a(E) = \sigma_0 e^{-\alpha\epsilon} = \sigma_0 e^{-\alpha(E-E_T)}$ where σ_0 is identified with the low-signal cross section. Molecules in energy shell E have a net absorption cross section $\sigma_{net}(E) = \sigma^a(E) - \sigma^e(E)$. By using the above assumptions it follows that

$$\sigma_{net}(E) = \sigma_0 e^{-\alpha(E-E_T)}\left[1 - e^{\alpha h\nu}\frac{g(E - h\nu)}{g(E)}\right] \qquad (3)$$

We now link this expression with experiment, showing that $\sigma_{net}(\bar{E}) \approx \sigma^{exptl}(F)$ for the situation in which the absorption is fluence rather than intensity dependent, i.e., $\bar{n}$ depends upon F but not on the pulse time τ. First note that although the "optical depth" problem has been removed in eq 1 and thus in eq 2 as well, $\bar{n}$ is still an ensemble averaged quantity. Thus $\bar{E}$, the average energy of the system, is given by

$$\bar{E} = \bar{n}h\nu + E_T \qquad (4)$$

Through this equation and eq 1 there is a one-to-one correspondence between F and $\bar{E}$. This means the cross section in eq 2 can be associated with a given $\bar{E}$ and we write

$$\sigma^{exptl}(F) = \sigma^{exptl}(\bar{E},\tau) = h\nu(\mathrm{d}\bar{n}/\mathrm{d}F)_{\bar{E},\tau} \qquad (5)$$

In our experiments the fluence is varied by changing the intensity I with τ constant. The fluence can also be varied by changing τ at constant I. In this case

$$\sigma^{exptl}(\bar{E},I) = h\nu(\mathrm{d}\bar{n}/\mathrm{d}F)_{\bar{E},I} \qquad (6)$$

In terms of the net microscopic cross sections associated with individual energy shells $\sigma^{exptl}(\bar{E},I) = (h\nu/I)\,(\mathrm{d}\bar{n}/\mathrm{d}t) = \int_{E_T}^{\infty}\sigma_{net}(E)p(E)\,\mathrm{d}E$, where $p(E)\,\mathrm{d}E$ is the fraction of molecules with energies in the range $(E, E + \mathrm{d}E)$. The evaluation of $p(E)$ in general requires rather detailed numerical computations.[3] But this can usually be avoided since over the range in which $p(E)$ has a significant contribution[13] $\sigma_{net}(E)$ is a relatively slowly varying function of E which can be replaced by a simple linear relationship $\sigma_{net}(E) = a + bE$. Under these conditions the above integral becomes $a + b\bar{E} = \sigma_{net}(\bar{E})$, where the latter is the microscopic cross section for molecules with energy $\bar{E}$, the average energy of the ensemble. The validity of such a treatment has been considered in greater detail recently by Grunwald et al.[10] Finally we note that a fluence rather than intensity dependence of the absorption requires that at a given fluence $(\mathrm{d}\bar{n}/\mathrm{d}F)_{\bar{E},\tau} = (\mathrm{d}\bar{n}/\mathrm{d}F)_{\bar{E},I}$ so that finally we have the desired link between experimental and model cross sections given by eq 2 and 3, respectively, viz., $\sigma^{exptl}(F) \approx \sigma_{net}(\bar{E})$. It is important to note that a differential cross section such as is given by eq 6 reflects the absorption associated with the energy distribution (average energy $\bar{E}$) obtained at the termination of the pulse of fluence F. In contradistinction an integral cross section defined by $(h\nu)\bar{n}/F$ includes absorption during the whole pulse and so reflects a complex averaging over time varying distributions among the various energy shells (Figure 4).

Experimental cross sections normalized relative to σ_0^{exptl} are plotted as points in Figure 5 for NH_3, SiF_4, C_4H_6O, and C_6F_6 and fluences in the range 0.03–0.8 J/cm^2. Also shown as full lines are $\sigma_{net}(\bar{E})$ curves obtained from eq 3. They are also normalized with respect to σ_0^{exptl} ($=\sigma_0$). Densities of states were calculated by the Haarhoff method[27] in conjunction with the known vibrational frequencies, while the various thermal vibrational energies, E_T, were also calculated by standard statistical techniques using the same frequency data. Other relevant information is given in Table I.

The following points may be noted. (a) In all cases $\sigma^{exptl}(\bar{E})$ decreases with energy. In terms of the model this can arise from (i) the tendency of the ratio $g(E - h\nu)/g(E)$ to increase toward

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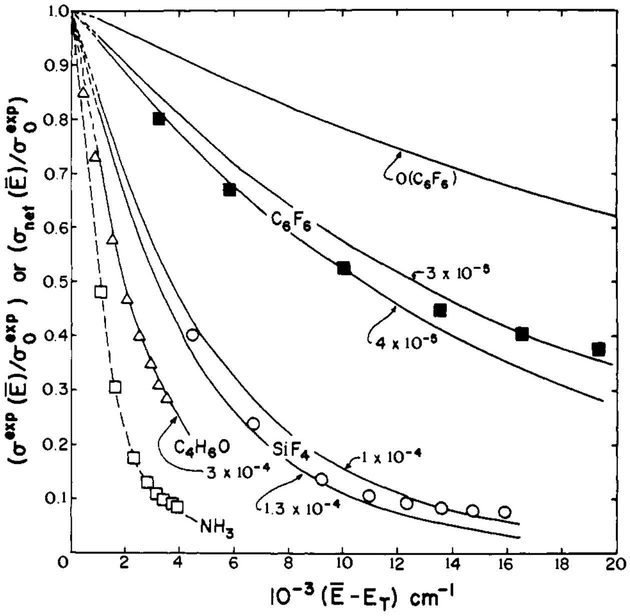

Figure 5. Experimental cross sections and net absorption cross sections as functions of vibrational energy ($\bar{E}$). E_T is the thermal vibrational energy before excitation. Points are experimental values for NH_3 (□), C_4H_6O (△), SiF_4 (○), and C_6F_6 (■) obtained from A_1, A_2, and B_1 parameters in conjunction with eq 1 and 2. The absorption parameters for C_6F_6, 7.1 torr, and C_4H_6O, 2.0 torr, are given in section 2b. For SiF_4 a pressure of 40 torr was assumed and the parameters were obtained from Figure 3. For ammonia the pressure was 200 torr and the values were taken from ref 2, viz., A_1 = 3.89 cm^{-1}, A_2 = 2.75 cm J^{-1}, and B_1 = 10 cm^2 J^{-1}. The experimental low-signal cross sections are given in Table I. Model curves using eq 3 are shown as full lines; each is identified by the α (cm) value used.

Table I. Absorption Data

	NH_3	SiF_4	C_4H_6O	C_6F_6
laser frequency, cm^{-1}	1076.0	1025.3	1073.3	1023.2
	(R 16)	(P 42)	(R 12)	(P 44)
band maximum, cm^{-1}	1076.0[a]	1032	1074	1020
fwhm, cm^{-1}		14	2.8	35
$10^{19}\sigma_0^{exptl}$, cm^2 [b]	6.0[c]	29[d]	2.0	16
$10^{-3}E_T$, cm^{-1}	0.011	0.45	0.44	1.49
$10^4\alpha$, cm		1.3	3	0.4
density of vibrational states at ϵ = 6000 cm^{-1}, cm	0.025	300	8000	9×10^{8}
rotational constants, cm^{-1}	$A = 6.30$[e] $B = 9.94$	$B = 0.139$[f]	$A = 0.36$[g] $B = 0.16$ $C = 0.11$	$A = 0.017$[h] $B = 0.034$

[a] Reference 28. [b] Calculated from A_1 parameter, using eq 20. [c] At 200 torr. σ_0^{exptl} is pressure dependent, see ref 2. [d] At 40 torr. σ_0^{exptl} is pressure dependent, see Figure 8. [e] Reference 34. [f] Reference 35. [g] Reference 36. [h] Reference 17.

1 as E increases or (ii) a positive value of α which reflects a decrease in $\sigma^a(E)$ with increasing energy. The density of states effect can be seen in the curve for C_6F_6 for which α = 0. In all cases the observed rate of decrease in $\sigma^{exptl}(\bar{E})$ was too great to be accommodated by this effect alone and required $\alpha > 0$. A positive value of α is an assumption often made in modeling studies. (b) Although eq 3 affords a reasonable fit it is apparent that the predicted fall-off is too large at high energies where the model requires $\sigma^a(E) \rightarrow 0$. In fact it may be expected that as a molecule climbs the excitation ladder it will first experience a decreasing cross section until it reaches a region in which the density of states is so high and intramode couplings are so strong that the cross section remains essentially constant. In this respect it is not surprising that C_6F_6 with its high density of roto-vibrational states has a lower α than C_4H_6O. (c) If the above were the only consideration, α's for SiF_4 and C_4H_6O might be expected to be comparable (because of the similar densities of states) while in fact α for SiF_4 is somewhat smaller than that for C_4H_6O. However, as can be seen from Table I, SiF_4 was irradiated to the red of the $v = 0 \rightarrow 1$ band center while C_4H_6O (and C_6F_6) were irradiated on the high-frequency side. Figure 6 shows that anharmonicity can be more easily overcome in the former case. We therefore feel that for a particular molecule the value of α may be frequency dependent and we hope that future work will elucidate this. (d) We did not attempt to calculate an α for NH_3. The low density of states makes it doubtful that statistical assumptions which are implicit in equations like eq 3 are in any way valid for the molecule. However, it is clear that $\sigma^{exptl}(\bar{E})$ drops rapidly with energy in this case as well. (e) For both C_6F_6[9,10] and C_4H_6O,[4a] $\bar{n}$, at a given fluence, was found to be independent of pressure but the same is not true for NH_3 or SiF_4 (see next section). The data in Figure 5 and Table I are for pressures at which both NH_3 and SiF_4 are in their high-pressure regions, i.e., the $\bar{n}$ vs. P curves, have reached a plateau region (see Figure 7).

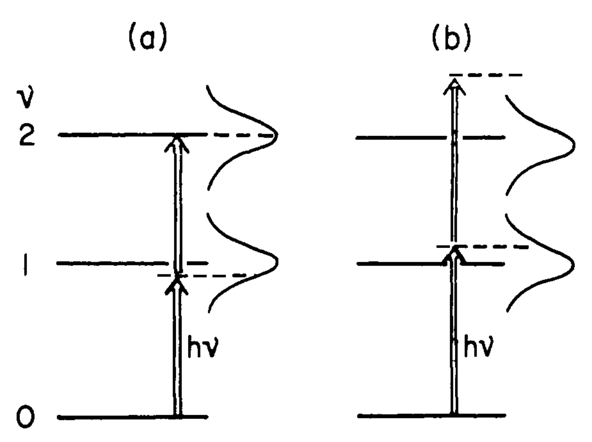

Figure 6. The effect of anharmonicity on absorption of photons tuned to (a) the high-energy region (b) the low-energy region of the 0–1 absorption band.

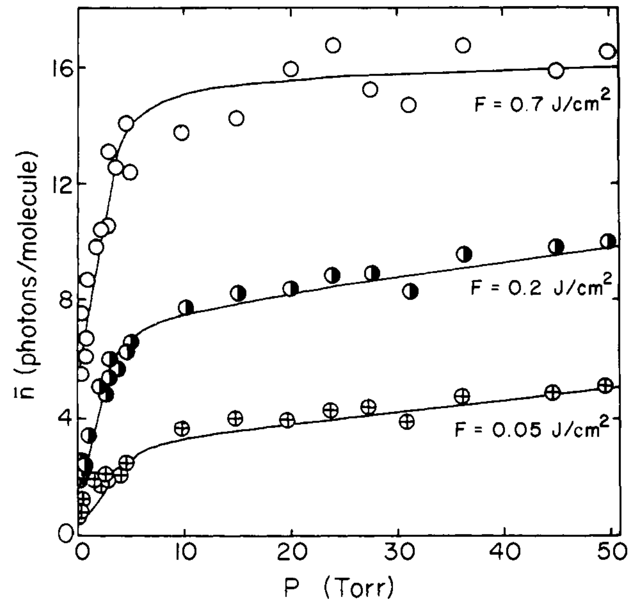

Figure 7. Photons absorbed per molecule ($\bar{n}$) as a function of pressure for SiF_4. Points are the values obtained by using eq 1 and experimental A_1, A_2, and B_1 parameters.

4. Pressure Dependence of Cross Sections and of $\bar{n}$. Although the extrapolated low-signal cross sections, σ_0^{exptl}, were found to be pressure independent for C_4H_6O and C_6F_6 the same is not true for SiF_4 (Figure 8) or for NH_3.[2] In the latter case our experimental values agreed very well with those obtained by Chang and

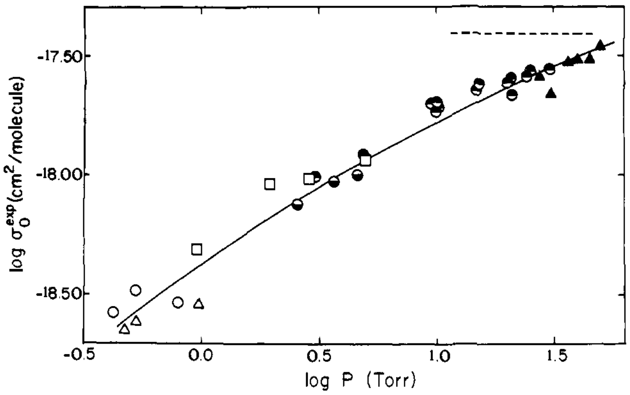

Figure 8. Low-signal absorption cross section of SiF_4 as a function of pressure. The coding for the points is the same as for Figure 3. The cross section obtained by using a standard 567 Perkin-Elmer infrared spectrometer, band pass 1.6 cm^{-1}, is shown as a dashed line.

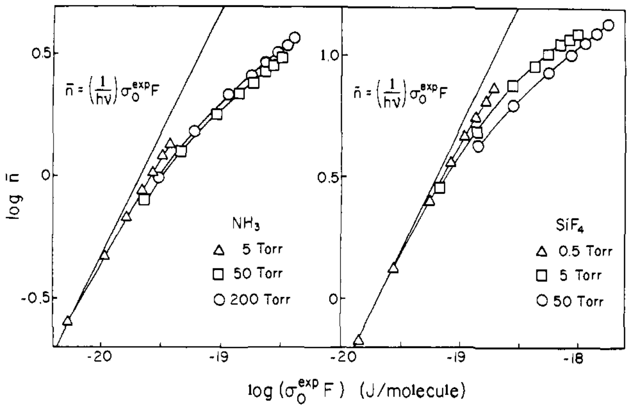

Figure 9. Photons absorbed per molecule ($\bar{n}$) as a function of $\sigma_0^{exptl}F$ where σ_0^{exptl} is the low-signal cross section (cm^2/molecule) and F (J/cm^2) is the fluence. Data for ammonia are from ref 2, and for SiF_4 from Figure 3.

McGee,[28] who carried out experiments under very low intensity conditions with use of a CW CO_2 laser. The pressure dependence arises from the small number of transitions lying close to the laser frequency and the broadening of these transitions with pressure. Presumably the same situation is occurring in SiF_4 although confirmatory low-intensity continuous wave laser studies have not been reported for this molecule. The absence of such effects in C_4H_6O and C_6F_6 is in agreement with the greater state congestion accompanying increased molecular complexity.

Judd[29] has made the very interesting observation for NH_3 that if $\bar{n}(P,F)$ is plotted vs. $\sigma_0^{exptl}F$ then to a good approximation our NH_3 data for different pressures fall onto a common curve. This is shown in Figure 9 for NH_3 and also for SiF_4. These results suggest that a major part of the pressure dependences in $\bar{n}(P,F)$, such as is shown in Figure 7 for SiF_4 and in ref 2 for NH_3, stems from the pressure dependence of the low-signal cross sections associated with pumping $v = 0 \rightarrow 1$ of the resonant mode. This is somewhat surprising since various other pressure effects not related to pressure broadening and hence to the pressure dependence of $\sigma_0(P)$ may also manifest themselves in the pressure dependence of $\bar{n}$. In particular for a small molecule like NH_3 with a large rotational spacing it is known[2] that only a small fraction ($f_r = 0.018$ for $\bar{\nu}_{irr} = 1076.0$ cm^{-1}) of the rotational levels in $v = 0$ are pumpable. These levels can only be replenished from the bath of rotational levels by collisions. Thus at low pressures in the absence of collisions the effective fraction of molecules which can be pumped, $\langle f \rangle$, is approximately equal to f_r.[4b,c] As pressure increases this effective fraction increases because molecules can be transferred from the bath to the active level(s) and so may begin their passage up the excitation ladder. Detail modeling[13] shows that this should result in a pressure dependence of $\bar{n}$ apart from any pressure dependence arising from σ_0. Collisions also result in V-V and V-T/R transfer which alters the vibrational distribution obtained under purely radiative conditions. This can have a very significant effect on the chemistry which "senses" the distribution in the high energy "tail".[3] The effect on the overall energy absorption is more modest. In terms of the previous section $\bar{E}$ will no longer equal $(\bar{n}h\nu + E_T)$ because some of the excitation energy will now be associated with translation and rotation. Pictorially collisions move molecules down the vibrational ladder and so into a region of possibly different effective absorption cross section. This means that cross sections derived by using eq 5 refer to vibrational energies which are somewhat less than $(\bar{n}h\nu + E_T)$. The exact magnitude will depend upon how rapidly V $\rightarrow$ T/R occurs as well as the magnitude of the effective heat capacities associated with the vibrational and translational-rotational modes. Such considerations have been discussed by us recently in what we have called a "thermal-conversion" model.[3]

Table II. Absorption Data at a Fixed Fluence[a]

molecule	pressure, torr	$\bar{n}$, photons/molecule	E_{abs}, kJ/mol	T_{eff}, K
NH_3	50	2.7	34	1170
	200	3.2	42	1310
SiF_4	5	13.4	164	2060
	50	12.9	158	2010
C_4H_6O	2	2.9	37	640
	6	3.1	40	660
C_6F_6	1	20	240	1360
	7	19	230	1330

[a] $F = 0.5$ J/cm^2 in all cases.

5. Factors Affecting the Efficiency of Reaction. Laser-induced chemical reactions may be effected by direct and by sensitized excitation.[11] In the latter case a sensitizer S becomes excited by interaction with the laser field. Energy transfer from the sensitizer to an acceptor A then excites the latter to a level from which it can react. A good sensitizer should (a) have a strong absorption at the laser frequency, (b) have a reasonably high vapor pressure, (c) be stable with respect to dissociation at the fluences employed, and (d) not interfere with the chemistry of A unless so desired. We have found that molecules like NH_3, SiF_4, and C_6F_6 satisfy most of these criteria. The first criterion also applies, of course, to direct excitation. The discussion in the previous sections now allows us to consider this criterion in somewhat greater detail.

(a) Low-Signal Cross Section. One of the most important factors determining the absorption strength is σ_0^{exptl}. (For complex molecules this is found to be reasonably close to the cross section determined by using a conventional spectrometer.) The effect of the low-signal cross section on absorption may be considered by comparing C_4H_6O and SiF_4 (Table II). Under the same fluence conditions SiF_4 absorbs more energy mainly because of its larger σ_0^{exptl}. In terms of direct reaction a molecule like C_4H_6O with $E_{act} = 52$ kcal/mol for its lower energy reaction pathway and with $\sigma_0^{exptl} = 2 \times 10^{-19}$ cm^2 (at 1073 cm^{-1}) shows negligible decomposition at an incident fluence of 0.5 J/cm^2 but this rises rapidly to 20% per pulse at 3.4 J/cm^2 for a pressure of $\sim$2 torr.[30] At the same pressure 1,1,2,2-tetrafluorocyclobutane with a spectroscopic cross section of 2×10^{-19} cm^2 (at 1055 cm^{-1}) and an activation energy of 70 kcal/mol for its lower energy reaction channel shows 30% decomposition at an incident fluence of 2.8 J/cm^2.[32] On the other hand, cyclopropane with a spectroscopic cross section of 4×10^{-20} cm^2 (at 1050 cm^{-1}) and activation energy of 65 kcal/mol requires >60 J/cm^2 to effect 1% reaction per pulse at 1 torr.[7] In general, for efficient direct reaction of molecules with reasonable activation energies at fluences $\sim$1 J/cm^2, σ_0^{exptl}

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[28] Chang, T. Y.; McGee, J. D. *Appl. Phys. Lett.* **1976**, *28*, 526.

[29] Judd, O. P., private communication.

[30] Yields are strongly pressure dependent, see ref 3 and 31.

[31] Koda, S.; Ohnuma, Y.; Ohkawa, T.; Tsuchiya, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3447.

[32] Selamoglu, N., unpublished results.

should be greater than 10^{-19} cm^2.

(b) Rate of Decrease of $\sigma_{net}(E)$. Although C_6F_6 has actually a smaller cross section than SiF_4 (Table I) it absorbs almost twice as much energy at the same fluence (Table II). This is attributable to the fact that $\sigma_{net}(E)$ decreases with energy more slowly in the case of C_6F_6 (Figure 5). If n vs. F curves for the two molecules are constructed, that for C_6F_6 shows smaller departure from linearity indicating $\sigma^{exptl}(F) \approx$ constant. In this sense it behaves as a pseudo-Lambert–Beer absorber.

(c) Heat Capacity. At reasonably high pressures (e.g., in sensitized systems) where thermalization competes with excitation it has proven useful to consider the system as having acquired an effective temperature (T_{eff})[6,33] at which reaction may occur. In this respect the amount of energy absorbed must be considered in conjunction with the heat capacity of the system. T_{eff} is defined through the equation $E_{abs} = \int_{298}^{T_{eff}} C_v \, dT$ where E_{abs} is the absorbed energy and C_v is the heat capacity of the system. As an example, compare SiF_4 and C_6F_6 (Table II). C_6F_6 absorbs more energy than SiF_4, yet it reaches a T_{eff} of only ~1350 K while SiF_4 reaches a T_{eff} of ~2050 K. This difference stems from the larger heat capacity of C_6F_6. On the other hand for the molecules SiF_4 and C_4H_6O which have rather similar heat capacities, values of T_{eff} are seen to follow the relative amounts of energy absorbed. Most marked is the case of C_6F_6 and NH_3 which have similar T_{eff} although C_6F_6 absorbs almost seven times as much energy. These effects can all be traced to the difference in C_v of the pairs compared.

6. Absorption Laws for Different Pulse Lengths and Higher Fluences. Equation 1 is a convenient way of summarizing the experimental data. Although it is often assumed that the temporal evolution is fluence rather than intensity dependent,[26] recent experimental data cast doubt on the generality of this.[5] This means that the values of the A_1, A_2, B_1, etc., parameters may be dependent on the nature of the pulse, in particular pulse length (as well as upon pressure). Under these circumstances, provided $\sigma_{net}(E)$ still decreases with increasing E, we in general have $\sigma^{exptl}(F) \lesssim d\int_{E_T}^{\infty} \sigma_{net}(E)p(E)\, dE$.

Also notice that although at moderate fluences $\bar{n} \propto F^m$ with $m < 1$ (see Figure 9), at the highest fluences the exponent of fluence reverts to unity in eq 1. However, most evidence indicates that at very high powers $m < 1$. Indeed recent measurements on SiF_4 at high fluences (>2 J/cm^2)[32] have shown that eq 1 predicts values of n higher than those actually observed. This suggests that the term A_2F^2 in eq 1 should be replaced by $A_2'F^{(1+x)}$ where $x < 1$ and is probably close to $^2/_3$.[4b]

Conclusions and Summary

For fluences ~1 J/cm^2 experimental data can be conveniently summarized in terms of parameters A_1, A_2, and B_1 associated with an empirical differential absorption law (eq 1). The data can also be conveniently expressed in terms of $\sigma^{exptl}(F)$. This differential cross section at fluence F can in turn be related, through a simple model for multiple photon excitation, to the net microscopic cross section associated with the "energy shell" of energy E. In the limit of low fluence, $\sigma^{exptl}(F)$ becomes the low-signal absorption cross section σ_0^{exptl}.

All molecules studied have $\sigma_{net}(E)$ decreasing with increasing E. The factors influencing this dependence include anharmonicity as well as molecular complexity.

In laser chemistry the nature and extent of reaction depend strongly upon E_{abs} and, under conditions in which molecules can be regarded as reaching an effective temperature, upon T_{eff}. The efficiency with which molecules harvest energy from the laser field will depend not only upon σ_0^{exptl} but also upon the rate of decrease of $\sigma_{net}(E)$. In addition T_{eff} will also reflect the effective heat capacity of the system.

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Infrared Multiphoton Absorption by Medium-Sized Molecules in the Gas Phase. Hexafluorobenzene and 2,3-Dihydropyran[†1]

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Abstract: Multiphoton IR absorption by C_6F_6 at 1023 cm^{-1} and by C_5H_8O at 1072 cm^{-1} was found to be independent of pressure and square-pulse equivalent (SPE) pulse width under the following conditions. For C_6F_6: P, 0.257–10.1 torr; SPE width, 80–330 ns; fluence, 0–0.7 J cm^{-2}; E_{abs}, 0–300 kJ/mol. For C_5H_8O: P, 11–36 torr; SPE width, 0.37–1.45 μs; fluence, 0–1.0 J cm^{-2}; E_{abs}, 0–130 kJ/mol. It is argued that the relative simplicity of these absorption laws, especially for C_6F_6, is related to physical properties generally shared by medium-sized and large molecules. A model is presented which reproduces the data for the present substrates with just one specific parameter. Results are also reported for IR absorption by SiF_4–C_5H_8O mixtures.

Basic knowledge of multiphoton absorption from high-power infrared laser sources is important to the control and interpretation of IR laser photochemistry. For small molecules an impressive amount of information is available, and convenient systematics for describing multiphoton absorption has been developed.[2-5] The phenomenology for small molecules is complicated. Absorption cross sections depend not only on temperature (or specific vibrational excitation) but also on pressure, intensity, and IR pulse shape.[2-5]

[†] Dedicated to George S. Hammond on the occasion of this 60th birthday.

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