

## THE FREQUENCY AND PRESSURE DEPENDENCE OF THE ABSORPTION OF PULSED CO<sub>2</sub> LASER RADIATION BY PHOSPHINE<sup>†</sup>

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### Summary

Absorption of IR radiation from a high power CO<sub>2</sub> laser by phosphine has been studied. At a constant pressure of phosphine, the fraction of energy absorbed is characteristic of the laser frequency. For a fixed laser frequency and constant incident intensity the pressure dependence of the optical density can be approximated by an empirically modified Beer-Lambert law. The effect of an added non-absorbing gas on the absorption coefficient of phosphine can be expressed simply by the addition of an appropriate term to the modified Beer-Lambert equation. Both dependences represent a phenomenological description of the effect of collisions on the IR multiphoton absorption process.

### 1. Introduction

The availability of high power lasers has opened up new areas of investigation in IR multiphoton photochemistry and spectroscopy. As might be expected, however, some difficulties regarding the interpretation of the mechanism of the multiphoton absorption process, as well as the mathematical descriptions of the process, have appeared [1]. Numerous observations have revealed that the process of multiphoton absorption obeys rather poorly the single-photon selection rules [2]. Moreover, the Beer-Lambert law has been found to be invalid under the prevailing high radiation density conditions. Spectroscopic investigations in the IR region have demonstrated that, under high radiation density conditions, the absorption coefficient no longer depends solely on the energy of the incident quanta but also depends on the incident intensity  $I_0$  (in watts per square centimeter) [3, 4], the

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incident fluence  $F_0$  (in joules per square centimeter) [5 - 16], the pressure  $P$  of absorbing molecules [4, 5, 7, 10 - 15, 17 - 20], the pressure  $P_F$  of foreign substances [5, 9, 11, 12, 15, 17, 18, 21, 22] and the temperature  $T$  [12, 19, 23].

In the present work investigations of the effect of frequency, pressure and the presence of foreign substances on the IR multiphoton absorption process in phosphine were undertaken. Phosphine appears to be an appropriate compound for this study because it is a small polyatomic molecule, does not decompose in the field of the unfocused laser beam [24] and has two normal vibrational modes  $\nu_2$  and  $\nu_4$ , whose fundamental frequencies lie in the emission region of the CO<sub>2</sub> laser [25, 26].

## 2. Experimental details

The IR multiphoton absorption measurements were carried out in a stainless steel cell fitted with NaCl windows and with an optical path length of 15.5 cm (volume, 152 cm<sup>3</sup>). The amount of energy  $E_{\text{abs}}$  absorbed by the gas and the incident pulse energy  $E_0$  were measured by means of a Gen-Tec (model ED-500) joulemeter. With the exception of the lower curve in Fig. 1, all incident and transmitted doses were corrected for reflection and absorption losses at the windows. All absorption measurements were made at ambient temperature (about 293 K).

The source of IR radiation was a pulsed CO<sub>2</sub> transversely excited atmospheric pressure laser (Lumonics model 103-2). The central portion of the laser beam was stopped down to an area of 2 cm<sup>2</sup> by a metal aperture. The laser was operated at 0.5 Hz with the following lasing gas mixture: 68% He, 23% CO<sub>2</sub> and 8% N<sub>2</sub>.

The single-photon (*i.e.* low intensity) IR transmission spectrum of phosphine was recorded on a Perkin-Elmer model 580 IR spectrometer.

Phosphine, helium and nitrogen, all of purity stated to be better than 99.9%, were obtained from the Matheson Company and were used as received. All gas mixtures were prepared using a Saunders-Taylor apparatus [27].

## 3. Results and discussion

### 3.1. Single-photon and multiphoton spectra

The low intensity IR transmission spectrum of gaseous phosphine in the frequency region of the  $\nu_2$  and  $\nu_4$  fundamental vibrational modes is presented as the upper curve in Fig. 1. The lower curve in this figure shows the absorption of energy by phosphine as a function of the available CO<sub>2</sub> laser frequencies. This latter spectrum was obtained using the unattenuated laser beam and hence the energy fluence varied from line to line [28] (Table 1). Since the high intensity absorption cross section usually depends on the

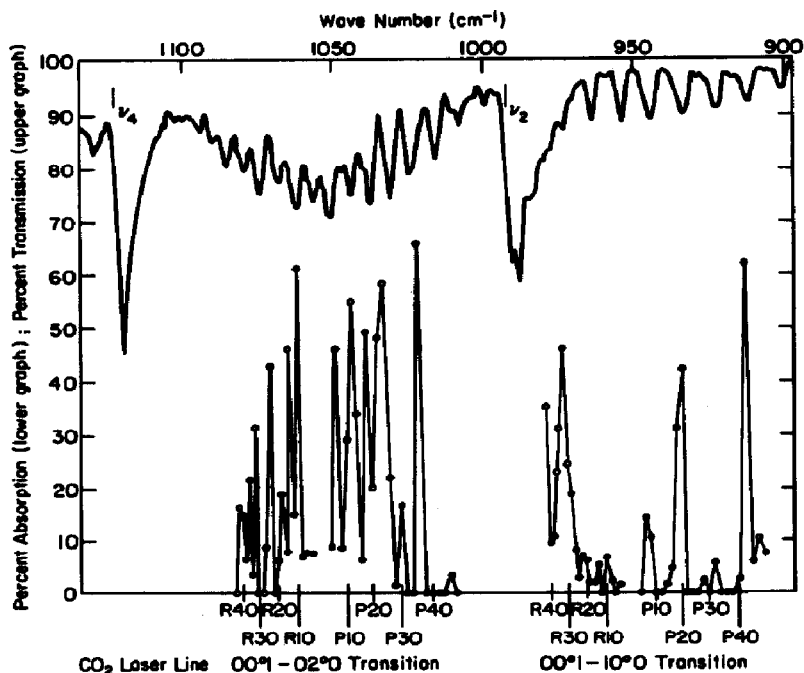


Fig. 1. The single-photon transmission spectrum of phosphine in a 10 cm cell as a function of wavenumber and the multiphoton absorption spectrum (○) in a 15.5 cm cell as a function of the CO<sub>2</sub> laser line ( $P(\text{PH}_3) = 50$  Torr). The multiphoton absorption data are arbitrarily joined by straight lines to guide the reader's eye.

TABLE 1

Absorption parameters for phosphine

Laser Wave line frequency [25] (cm <sup>-1</sup> )	Incident fluence (J cm <sup>-2</sup> )	Frequency mismatch $\nu_{\text{laser}} - \nu_0^a$ (cm <sup>-1</sup> )	Absorption cross section <sup>b</sup> ( $\times 10^{-20}$ cm <sup>2</sup> molecule <sup>-1</sup> )	Constants in eqns. (1) and (2)		$n$	Constants <sup>d</sup> in eqns. (3) and (4)	
				A	B		C (cm <sup>-1</sup> Torr <sup>-1</sup> )	m
P42	922.914	0.35	3.4	0.0012	0.00090	0.66	0	0
P20	944.194	0.80	1.9	0.0040	0.00031	0.94	0.00084	0
R32	983.252	0.70	2.6	0.0027	0.00028	0.57		
P36	1031.477	0.60	4.0	0.0041	0.00090	0.87	0.00099	0
P24	1043.163	0.70	3.0	0.0029	0.00028	0.52		
P12	1053.924	0.70	2.5	0.0012	0.00058	0.60		
R14	1074.646	0.80	2.1	0.0019	0.00015	0.47	0.00083	0

<sup>a</sup>For information see text.

<sup>b</sup>At 50 Torr of PH<sub>3</sub> and ambient temperature (298 K).

<sup>c</sup>Double-degenerate transition in phosphine.

<sup>d</sup>Evaluated at a PH<sub>3</sub> pressure of 30 Torr.

incident energy fluence [5 - 16], the multiphoton absorption spectrum (lower curve in Fig. 1) is meaningful for the actual experimental conditions only; at a constant fluence we would expect a somewhat different picture. This fact makes the interpretation of the spectral data more difficult, but nevertheless a number of significant observations can be made.

A rough comparison of the spectra shown in Fig. 1 indicates that no general correlation exists between the single-photon low resolution IR spectrum of phosphine and that characterizing the absorption of intense laser radiation. Such a procedure may not, however, be the best one for comparison of these kinds of spectral characteristics. As the laser radiation is highly monochromatic it is more appropriate to compare the high fluence laser spectrum of phosphine shown in Fig. 1 with a single-photon high resolution spectrum of the compound. Indeed, strong absorption is observed when the difference between the frequency  $\nu_{\text{laser}}$  of a given laser line [26] and the frequency  $\nu_0$  of the vibration-rotation transition in phosphine [25] closest to it is relatively small (Table 1). If this difference becomes fairly large no absorption is observed. However, some deviations from this qualitative rule are found. As a characteristic example, we may consider the P12 line of the  $00^{\circ}1-02^{\circ}0$  transition. Despite a fairly large frequency mismatch (Table 1), this emission line of the laser is strongly absorbed by phosphine. It may also be noted that an increase in the degeneracy of a given vibration-rotation transition causes an increase in the multiphoton absorption coefficient. These facts clearly indicate that the process of multiphoton absorption of  $\text{CO}_2$  laser radiation in phosphine is mainly of a resonant nature.

In analysing the multiphoton absorption spectrum in Fig. 1, we notice that the tendency of phosphine to absorb laser radiation varies with the emission region of the  $\text{CO}_2$  laser. Generally, lines belonging to the P and R branches of the  $00^{\circ}1-02^{\circ}0$  laser transition are absorbed more strongly and more frequently than those arising from the  $00^{\circ}1-10^{\circ}0$  transition although the intensities of the pertinent lines of both emission bands are almost the same [28]. This presumably arises from the fact that the availability of vibration-rotation states in phosphine is higher for the former emission region of the laser [25]. In this former region (*i.e.*  $00^{\circ}1-02^{\circ}0$ ) both R and P rotational branches of the  $\nu_2$  and  $\nu_4$  vibrations respectively of  $\text{PH}_3$  occur. In contrast, only single rotational branches P and Q of the  $\nu_2$  mode of phosphine fall within the P and R emission regions respectively of the  $00^{\circ}1-10^{\circ}0$  transition of the laser [25, 26].

### 3.2. Pressure dependence of energy deposition

Absorption measurements generally yield averaged information over the sample dimensions. To investigate the pressure dependence of the amount of energy absorbed it is convenient to express it as the ratio  $E_{\text{abs}}/E_0$ . It is noticed immediately that the absorption data obtained at several frequencies show the same behavior; an example of this observed dependence is seen in Fig. 2. For all the emission lines investigated the fraction of energy absorbed initially increases sharply with an increase in the pressure and then

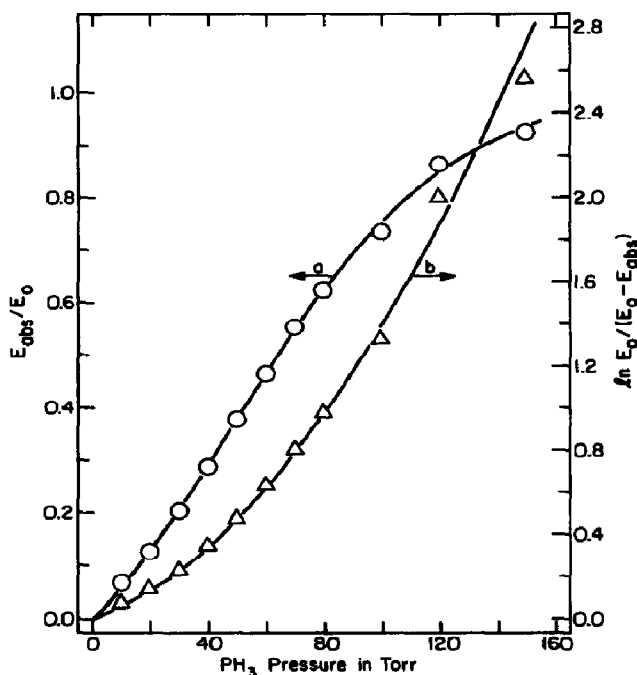


Fig. 2. Dependence of the fraction of energy absorbed per pulse (○) and the optical density (△) on the pressure of phosphine for the P20 line ( $944.2 \text{ cm}^{-1}$ ) (fluence,  $0.8 \text{ J cm}^{-2}$ ): —, calculated using the three constants  $A$ ,  $B$  and  $n$  determined by the optimization procedure described.

asymptotically approaches the maximum value of unity at the high pressure limit (Fig. 2, curve a). Plots of the logarithm of  $E_0/(E_0 - E_{\text{abs}})$  (optical density) *versus* pressure (Fig. 2, curve b) generally exhibit non-linear relationships that show positive deviations from the Beer-Lambert law. This type of dependence suggests that the data might be fitted by the expression [24]

$$\frac{E_{\text{abs}}}{E_0} = 1 - \exp\left[-\left\{A\left(\frac{P}{P_0}\right)^n + B\right\}LP\right] \quad (1)$$

where  $L$  denotes the optical path length,  $P$  is the pressure of phosphine and  $P_0$  is equal to 760 Torr (atmospheric pressure). To obtain the best test of the adjustable constants in eqn. (1) the values  $A$ ,  $B$  and  $n$  were first estimated by taking three experimental data points and were then optimized according to the simplex procedure [29] using the full set of data points. The values of the empirical parameters derived in this way for several laser lines are listed in Table 1. In addition, the full curves in Fig. 2 are calculated curves based on the derived constants  $A$ ,  $B$  and  $n$ . It is worth mentioning that a two-parameter equation of the type  $A(P/P_0)^n$  was not suitable for the approximation of absorption data in our case; it was found that plots of  $\ln(\text{optical density})$  *versus*  $\ln(P/P_0)$  were generally non-linear.

Although eqn. (1) presents a purely empirical relationship, some remarks regarding its physical meaning are warranted. The logarithmic form of eqn. (1) is

$$\ln\left(\frac{E_0}{E_0 - E_{\text{abs}}}\right) = \left\{ A\left(\frac{P}{P_0}\right)^n + B \right\} LP \quad (2)$$

Thus the quantity  $A(P/P_0)^n + B$  can be considered as an absorption coefficient, or absorption cross section, at a given fluence. The parameter  $B$  in eqn. (2) characterizes the multiphoton absorption of radiation at the low pressure limit, *i.e.* in collisionless conditions. However, the term  $A(P/P_0)^n$ , which is responsible for the non-Beer-Lambert behavior, describes an increase in the absorption coefficient caused by an increase in the density of absorbing molecules. Since the number of collisions increases with the square of the gas pressure or density, it is probable that this latter term arises from the effect of collisions on the IR multiphoton absorption process. The data listed in Table 1 indicate that the contribution of the  $A(P/P_0)^n$  term to the total value of the absorption coefficient is a feature characteristic of the laser line absorbed. For some laser frequencies the main contribution to the absorption coefficient arises from  $B$  (*e.g.* for the P42 and P12 lines); for others, the  $A(P/P_0)^n$  term dominates (*e.g.* for the R14 and P24 lines).

Plotting the value of the absorption coefficient against the pressure of phosphine always leads to concave curves, which means that  $n$  can vary between zero and unity. The upper limit of unity corresponds to the situation when the  $A(P/P_0)^n$  term in the optical density is directly proportional to the number of two-center collisions. If  $n$  is equal to zero then each isolated molecule absorbs radiation and collisions do not influence the absorption process. Of course, in this case the absorption coefficient becomes independent of  $P$  and we can expect  $A$  to be equal to zero. Presumably, for any value  $0 < n < 1$  only certain collisions affect the absorption process and thus the appropriate term in the optical density is not directly proportional to the number of collisions.

Similar dependences to those presented above have been observed in multiphoton absorption studies of other systems [4, 5, 7, 8, 10 - 15, 17 - 20] although some authors of the cited papers have proposed more complex forms of mathematical expressions for approximation of the experimental data.

### 3.3. Effect of a foreign gas on the multiphoton absorption process

Since an increase in the pressure of phosphine causes an increase in the absorption coefficient, it might be expected that a similar effect would occur when foreign gases are added. Indeed, the addition of helium, neon or nitrogen at a constant pressure of phosphine usually causes an increase in the amount of energy deposited. This phenomenon was investigated thoroughly for the case of helium and the results of these studies are presented as points in Fig. 3. For other bath gases investigated it was generally observed that the larger is the collision diameter, the more pronounced is the effect on the multiphoton absorption process.

In considering an appropriate expression for the description of the multiphoton absorption of IR radiation in this case, we conclude that the

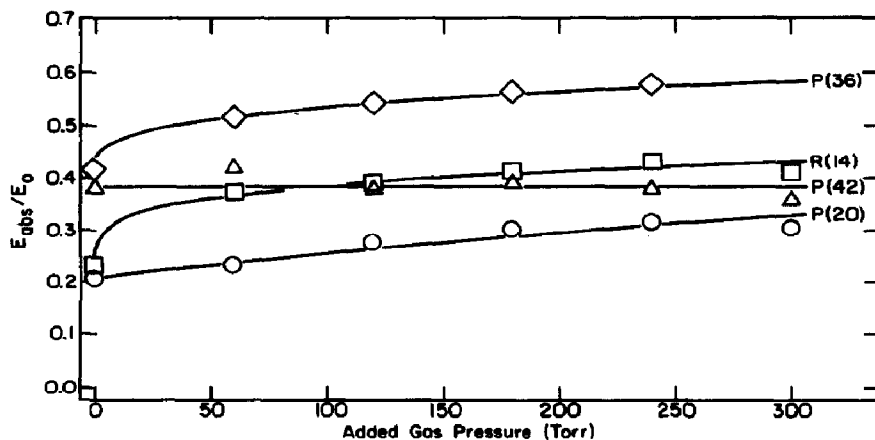


Fig. 3. Dependence of the fraction of energy absorbed per pulse by phosphine on the partial pressure of helium ( $P(\text{PH}_3) = 30$  Torr).

most convenient is a modification of eqns. (1) and (2) by the addition of an appropriate term to the absorption coefficient. This term, introduced according to the absorption additivity law, should describe a possible increase in the amount of energy absorbed caused by collisions of the absorbing molecules with molecules of the foreign bath gas. Thus, in the presence of a bath gas, expression (2) takes the form

$$\ln \left\{ \frac{E_0}{(E_0 - E_{\text{abs}})_F} \right\} = \left\{ A \left( \frac{P}{P_0} \right)^n + B + C \left( \frac{P_F}{P_0} \right)^m \right\} LP \quad (3)$$

where subscript F denotes a foreign gas. It can be shown that the combination of eqns. (2) and (3) can be written in the form

$$\ln \left[ \ln \left\{ \frac{E_0 - E_{\text{abs}}}{(E_0 - E_{\text{abs}})_F} \right\} \right] = \ln(CLP) + m \ln \left( \frac{P_F}{P_0} \right) \quad (4)$$

Values of the constants  $C$  and  $m$  giving the best fit of eqn. (3) to the experimental results shown in Fig. 3 are listed in Table 1. They were derived from eqn. (4) by applying a least-squares method. The constants  $C$  and  $m$ , similar to  $A$ ,  $B$  and  $n$ , are characteristic of a given laser frequency. The  $m$  values should also vary between zero and unity, and this is confirmed by our experimental data (Table 1). It is interesting, however, that absorption of the P42 line is not affected by the presence of helium.

The effect of the presence of a foreign bath gas on the multiphoton absorption process has been studied by several research groups [5, 9, 11, 13, 15, 17, 18, 21, 22]; to our knowledge, however, no reports involving a phenomenological description of the process have yet appeared.

The effect of the pressure and the presence of a bath gas on the multiphoton absorption process is still not well understood. One possible explanation of this effect might be that collisions cause broadening of the vibration-

rotation states of the absorbing molecule [5]. A second possibility is that, with an increase of pressure, vibration-translation and vibration-rotation relaxation rates increase [5, 9, 13, 18, 23]. Finally, if the collision partner for an absorbing molecule is sufficiently large and complex, intramolecular vibration-vibration energy transfer may occur [18, 21]. Undoubtedly, any of these processes will help to overcome the bottleneck for the IR multiphoton absorption process and thus will cause an increase in the amount of energy absorbed.

#### 4. Further remarks

Equations (1) and (3) must be simpler forms of a more general relationship expressing the amount of energy absorbed as a function of all the parameters influencing the multiphoton absorption process. Unfortunately, none of the equations proposed in the literature [5, 7 - 10, 18] can be reduced to the simpler forms we have presented.

By analogy with the low intensity behavior of absorbing systems it can be assumed that the process of multiphoton absorption is governed by the empirical differential law

$$\frac{dI}{dL} = -\epsilon L \quad (5)$$

where  $I$  represents the actual pulse intensity at a given depth in the absorbing system and  $\epsilon$  is the absorption coefficient. Absorption of the electromagnetic radiation under the low intensity conditions is accomplished in such a way that  $\epsilon$  remains practically constant. In this case eqn. (5) can easily be integrated leading to the well-known Beer-Lambert expression. Since, as was mentioned earlier, the amount of energy deposited in the multiphoton absorption can be affected by several factors, one way to handle the problem is to make  $\epsilon$  dependent upon all of them. Thus, at constant temperature and for a given laser frequency, the absorption coefficient can be expressed by the empirical relationship

$$\epsilon = \epsilon_0 \frac{1 + \{A'(P/P_0)^n + B' + C'(P_F/P_0)^m\}(I_0/I_c)^a}{1 + (I_0/I_c)^a} \quad (6)$$

where  $\epsilon_0$ ,  $A'$ ,  $B'$ ,  $C'$ ,  $I_c$ ,  $n$ ,  $m$  and  $a$  are constants and  $I_0$  is the incident pulse intensity. The other symbols have been defined earlier. The constants  $I_c$  and  $P_0$  have been introduced to render the appropriate power expressions dimensionless. Of course, if the pulse duration is kept constant, the pulse fluence  $F_0$  or the pulse energy  $E_0$  can be used instead of  $I_0$ .

The absorption coefficient expressed by eqn. (6) is dependent on the incident pulse intensity only and thus the integrated expression takes the very simple form

$$\ln\left(\frac{I_0}{I_0 - I_{\text{abs}}}\right) = E_0 \frac{1 + \{A'(P/P_0)^n + B' + C'(P_F/P_0)^m\}(I_0/I_c)^a}{1 + (I_0/I_c)^a} LP \quad (7)$$



This approach seems to be more convenient than that proposed by Starov and coworkers [7, 10]. These workers assumed  $\epsilon$  to be dependent on the actual energy of the pulse at a given depth. This requires, for more precise calculations, the application of rather complicated integration procedures. Moreover, the equation proposed by these workers describes only the dependence of  $\epsilon$  on the laser intensity. The parameters derived by this method are functions of the pressure of absorbing molecules and probably also of the pressure of buffer gas added [10]. A similar approach has been described by Lussier *et al.* [5].

A more general method has been proposed by Lyman *et al.* [8]. These workers assumed a fairly simple functional dependence of the multiphoton absorption cross section on the incident fluence and the pressure of the absorbing species. Unfortunately the integrated form based on this equation does not reduce to the simple Beer-Lambert law under low fluence conditions. Furthermore, the expression does not account for the dependence of the absorption cross section on the presence of a foreign bath gas.

Let us consider now the behavior of eqns. (6) and (7) under the boundary conditions.

(1) When  $I_0$  approaches zero, *i.e.* at low incident radiation intensity,  $\epsilon$  approaches  $\epsilon_0$  and eqn. (7) reduces to the simple Beer-Lambert law. Thus  $\epsilon_0$  in eqn. (6) can be identified with the classical absorption coefficient.

(2) At high incident radiation intensity ( $I_0 \rightarrow \infty$ )

$$\epsilon = \epsilon_{\text{sat}} = \epsilon_0 \left\{ A' \left( \frac{P}{P_0} \right)^n + B' + C \left( \frac{P_F}{P_0} \right)^m \right\}$$

Thus eqn. (7) predicts saturation of the optical density under high power, and this is actually observed in multiphoton absorption studies [1, 7, 8, 10]. As the absorption can be affected by collisions,  $\epsilon_{\text{sat}}$  and the optical density given by eqn. (7) should increase with an increase in the pressure of absorbing molecules and/or the pressure of the foreign gas added. This phenomenon has been also observed experimentally [7, 8, 10]. Of course, under collisionless conditions  $\epsilon_{\text{sat}}$  will reduce to the form  $\epsilon_0 B'$ .

(3) If  $I_0$  is equal to  $I_c$ ,  $\epsilon = \frac{1}{2} \epsilon_0 + \frac{1}{2} \epsilon_{\text{sat}}$ .

(4) At a constant incident energy fluence eqn. (7) reduces to eqn. (2) or eqn. (3).

(5) At a constant pressure of absorbing molecules and a constant pressure of a bath gas

$$\epsilon = \epsilon_0 \left\{ 1 + \text{constant} \times \left( \frac{I_0}{I_c} \right)^a \right\} \left\{ 1 + \left( \frac{I_0}{I_c} \right)^a \right\}$$

Thus eqn. (7) represents a saturation-type relationship.

All features of the approach we have described indicate that it should be very convenient for the empirical description of multiphoton absorption in the IR region.

Reviewing the data shown in Table 1, we notice that phosphine absorbs radiation from a non-focused CO<sub>2</sub> laser beam rather weakly. The value of the absorption cross sections are more than an order of magnitude lower than those for SiF<sub>4</sub> [10, 24], SF<sub>6</sub> [8], SiH<sub>4</sub> [30] and even NH<sub>3</sub> [7, 10]. One possible explanation of this fact is that the density of states in PH<sub>3</sub> is much lower than that in the case of more complex molecules [10]. Another is that the relaxation processes are slow. Both these factors would make it more difficult for the molecule to overcome anharmonicity.

The low absorptivity of phosphine could explain the surprisingly high resistivity of the compound to the action of non-focused CO<sub>2</sub> laser radiation. According to Starov *et al.* [10], to observe noticeable decomposition of a compound it is necessary that its absorption cross section be greater than 10<sup>-19</sup> cm<sup>2</sup> molecule<sup>-1</sup> at a fluence of about 1 J cm<sup>-2</sup>. This is never attained in the case of phosphine. This could also account for the difference between the behavior of phosphine [24, 31, 32] and silane [30 - 32] during interaction with the high power laser field. Despite almost the same thermochemical requirements for the decomposition of both silane and phosphine, only the former dissociates easily in a non-focused laser beam.

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### References

- 1 W. Fuss and K. L. Kompa, *Prog. Quantum Electron.*, 7 (1981) 117.
- 2 S. E. Bialkowski and W. A. Guillory, *Chem. Phys.*, 55 (1981) 229.
- 3 M. N. R. Ashfold, C. G. Atkins and G. Hancock, *Chem. Phys. Lett.*, 80 (1981) 1.
- 4 D. K. Evans, R. D. McAlpine, H. M. Adams and A. L. Creagh, *Chem. Phys.*, 80 (1983) 379.
- 5 F. M. Lussier, J. I. Steinfeld and T. F. Deutsch, *Chem. Phys. Lett.*, 58 (1978) 277.
- 6 B. G. Gowenlock, P. John, R. Leo, R. G. Harrison, S. Butcher and C. Steel, *J. Photochem.*, 9 (1978) 200.
- 7 V. Starov, C. Steel and R. G. Harrison, *J. Chem. Phys.*, 71 (1979) 3304.
- 8 J. L. Lyman, R. G. Anderson, R. A. Fisher and B. J. Feldman, *Chem. Phys.*, 45 (1980) 325.
- 9 J. B. Marling, I. P. Herman and S. J. Thomas, *J. Chem. Phys.*, 72 (1980) 5603.
- 10 V. Starov, N. Selamoglu and C. Steel, *J. Am. Chem. Soc.*, 103 (1981) 7276.
- 11 A. V. Eletskii, V. D. Klimov and I. A. Udalova, *Zh. Eksp. Teor. Fiz.*, 80 (1981) 558.
- 12 F. Duperrex and H. Van den Bergh, *J. Chem. Phys.*, 75 (1981) 3371.
- 13 D. K. Evans, R. D. McAlpine and H. M. Adams, *J. Chem. Phys.*, 77 (1982) 3551.
- 14 K. O. Kutschke, M. Gauthier and P. A. Hackett, *Chem. Phys.*, 78 (1983) 323.
- 15 N. Presser, J. R. Barker and R. J. Gordon, *J. Chem. Phys.*, 78 (1983) 2163.
- 16 V. M. Apatin and G. N. Makarov, *Zh. Eksp. Teor. Fiz.*, 84 (1983) 15.
- 17 W. A. Jalenak and N. S. Nogar, *Chem. Phys.*, 41 (1979) 407.
- 18 R. A. Gorber, R. E. McNair, S. F. Fulghum, M. S. Feld and B. J. Feldman, *J. Chem. Phys.*, 72 (1980) 4693.

- 19 U. Persson, B. Marthinsson, J. Johansson and S. T. Eng, *Appl. Opt.*, 19 (1980) 1711.
- 20 H. Stafast, J. Opitz and J. R. Huber, *Chem. Phys.*, 56 (1981) 63.
- 21 G. P. Quigley and J. L. Lyman, *Springer Ser. Chem. Phys.*, 6 (1979) 134.
- 22 R. T. Bailey, F. R. Cruickshank, D. Pugh and W. Johnstone, *J. Chem. Soc., Faraday Trans. II*, 77 (1981) 1387.
- 23 J.-S. J. Chou and E. R. Grant, *J. Chem. Phys.*, 74 (1981) 384.
- 24 J. Blazejowski and F. W. Lampe, *J. Phys. Chem.*, 88 (1984) 1666.
- 25 P. K. L. Yin and K. N. Rao, *J. Mol. Spectrosc.*, 51 (1974) 199.
- 26 J. Dupre-Maquaire and P. Pinson, *J. Mol. Spectrosc.*, 62 (1976) 181.
- 27 K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, 9 (1941) 616.
- 28 K. Walzer, M. Tacke and G. Busse, *J. Chem. Phys.*, 73 (1980) 3095.
- 29 D. E. Long, *Anal. Chim. Acta*, 46 (1969) 193.
- 30 P. A. Longeway and F. W. Lampe, *J. Am. Chem. Soc.*, 103 (1981) 6813.
- 31 J. Blazejowski and F. W. Lampe, *J. Photochem.*, 20 (1982) 9.
- 32 J. Blazejowski and F. W. Lampe, *J. Photochem.*, 24 (1984) 235.