

Collision induced deactivation of the bending mode $v=1$ vibrational level of the excited \tilde{A}^2A_1 and ground \tilde{X}^2B_1 electronic states of PH_2 by rare gases

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Collisional deactivation of the vibrational level $v=1$ of the bending mode by rare gases has been studied for both the excited \tilde{A}^2A_1 and ground \tilde{X}^2B_1 electronic states of PH_2 . Quenching constants have been determined. While a non-SSH behavior has been observed in the dependence of the relaxation probability upon the mass of the collision partner in the ground state denoting a possible predominance of an intramolecular $V-R$ energy transfer process, the cross sections fit quite well the Parmenter and co-workers' potential well depth correlation rule for both the electronic states indicating that their interactions with the quenchers occur for both of them under the influence of long range attractive forces. © 1997 American Institute of Physics. [S0021-9606(97)01518-3]

I. INTRODUCTION

Extensive spectroscopic studies conducted by Ramsay and co-workers¹ on the PH_2 radical have made it one of the most interesting triatomic molecules to investigate from the dynamic point of view. Recent work by Chen *et al.*² on PH_2 cooled in a supersonic jet, even if it points out some discrepancies in the wave number values of a certain number of assignments for the $(0,0,0-0,0,0)$, $(0,1,0-0,0,0)$, and $(0,2,0-0,0,0)$ bands of the $\tilde{A}^2A_1-\tilde{X}^2B_1$ electronic transition, practically confirms the results obtained at room temperature by the previous authors.

Single vibrational level time-resolved spectroscopy works were carried out on the PH_2 first excited electronic state \tilde{A}^2A_1 in the past³⁻⁵ in this laboratory. Radiative lifetimes and self-quenching constants have been measured for vibrational levels going from $v'_2=0$ to $v'_2=7$, i.e., to beyond the barrier to linearity. The occurrence of a predissociation process via coupling with the ground \tilde{X}^2B_1 electronic state and a dissociative 4A_2 state starting at $v'_2=4$ has been evidenced. An experimental setup using laser induced fluorescence (LIF) as a diagnostic technique and a VUV flash photolysis apparatus for the generation of electronic ground state PH_2 radicals from PH_3 was employed, which, however, due to electromagnetic interferences between the photolysis flashes and the detection system and to a low repetition rate did not allow us to deal with problems concerning the time evolution of vibrational populations of the PH_2 ground electronic state.

The PH_2 radical, despite the great amount of information concerning its spectroscopy, has so far been the object of only a relatively few number of studies. Laser photolysis of PH_3 was first investigated by Sam and Yardley⁶ which lead to the measurement of the radiative lifetimes and self-quenching constants of the vibrational levels $v'_2=0-4$ of $\text{PH}_2(\tilde{A}^2A_1)$ directly produced by the laser photolysis pro-

cess, the values of which however were not by us confirmed.³ To our knowledge, the second laser photodissociation study of PH_3 dealing with PH_2 was published by Wittig and co-workers.⁷⁻⁹ The kinetics and reactivity of the $v''_2=0$ species of the PH_2 ground electronic state were investigated in Ref. 9, even though this topic appeared more as a secondary aspect rather than the principal subject of the paper which was focussed on the internal energy distribution among the photofragments of PH_3 . Thus, unlike the other dihydride triatomic molecule NH_2 , PH_2 still is not well known from the dynamic and kinetic points of view at least for what concerns its ground electronic state vibrational species.

With this study we have investigated the deactivation due to collisions with added gases of the vibrational level $v_2=1$ of the bending mode of both the excited and ground electronic states of PH_2 , i.e., \tilde{A}^2A_1 and \tilde{X}^2B_1 , respectively. The rare gases were employed as collision partners.

In the above mentioned studies concerning the quenching of $\text{PH}_2(\tilde{A}^2A_1)$, only collisions with the parent molecule PH_3 were studied. The availability of deactivation data due to other quenchers would allow a comparison with existing theoretical models like those by Thayer and Yardley^{10,11} and by Parmenter and co-workers.^{12,13}

Collision induced relaxation of $\text{PH}_2(\tilde{X}^2B_1, v''_2=1)$ by rare gases should theoretically involve only a $V-T$ energy transfer process and the $V-V$ or reactive channels can be left aside. A correlation of the variation of the quenching efficiencies with the various colliders could thus hopefully be established with some degrees of complication less.

A great amount of work on the vibrational relaxation has been done for diatomic molecules and a certain number of triatomic or more complex molecules. While for molecules having large moments of inertia, usually molecular rotations are not considered in a $V-T$ process, for hydrogenated or deuterated molecules where the moments of inertia could be much smaller, rotation has been found to play a competitive

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role with respect to translation in the deactivation of vibrational energies.

Among triatomic molecules, vibrational relaxation studies have been carried out in a certain detail for CO₂, OCS, N₂O while to our knowledge little is known about hydride molecules except HCN for which extensive data have been gathered by Smith and co-workers^{14–18} and more recently by Bethardy *et al.*^{19,20} As to dihydrides, H₂O (Refs. 21, 22) and H₂S (Ref. 23) have been studied. NH₂ is another one of these few investigated dihydrides.

Xiang *et al.*²⁴ have found in the collision induced relaxation of NH₂(\tilde{X}^2B_1 , $v_2''=1$) that the probability of energy transfer does not strictly obey the Schwartz, Slawsky, and Herzfeld (SSH) (Ref. 25) mass law and an involvement of an efficient intramolecular *V–R* process has been invoked.

In studying the deactivation of PH₂(\tilde{X}^2B_1 , $v_2''=1$) we hope to contribute to get more information about the behavior of dihydride triatomic molecules and a comparison of its relaxation data with those of NH₂ which has the heavier atom belonging to the same group might shed some more light on the mechanisms responsible for the vibrational deactivation of both these molecules.

The laser induced fluorescence technique employed to observe the time-resolved emission decay of the PH₂ excited electronic species and to measure their quenching constants due to collisions with the rare gases, allowed at the same time to probe the populations of PH₂(\tilde{X}^2B_1 , $v_2''=1$) by collecting the total fluorescence signals.

II. EXPERIMENT

The PH₂ species were generated from the photofragmentation of PH₃ by an ArF excimer laser and the time evolution of their populations was monitored by the LIF technique with a dye laser.

The reactions occurred in a vessel made of black anodized aluminum of $\sim 750\text{ cm}^3$ provided with lateral arms of 15 cm long and 2 cm of diameter for the entrance and exit of the laser beams which were set at right angles to each other. Particular care was devoted to the design of the LIF laser arms in order to reduce to the lowest level the ambient light filtering in and especially the laser scattering which otherwise could cause severe interference to the fluorescence signals. They were in fact supplied with light baffles internally and the exit arm was equipped with a Brewster angle window. Besides, a collimator of 3 mm of diameter was mounted in front of the entrance window to let in only the core of the laser beam. Suprasil windows were used.

The photolysis laser was a Lambda Physik Model EMG 150 TMSC excimer laser which was made to work as an ArF laser producing 193 nm wavelength radiation. Outputs with spot of approximately 1 cm² were obtained by narrowing the rear mirror iris and energies of 5–15 mJ per pulse were measured. The laser beam was directed into the reaction cell without focusing. The pulse width is $\sim 15\text{ ns}$ FWHM.

A Quanta Ray Model PDL1 dye laser pumped by a Quanta Ray Model DCR1A Nd:YAG laser, was used to perform laser induced fluorescence on ground state PH₂

radicals. The monitoring of PH₂(\tilde{A}^2A_1 , $v_2'=1$) and PH₂(\tilde{X}^2B_1 , $v_2''=1$) concentrations was obtained through excitation of the PH₂(\tilde{A}^2A_1 , $v_2'=1-\tilde{X}^2B_1$, $v_2''=1$) system and in particular of the RQ_0 (6₁₆–6₀₆ and 4₁₄–4₀₄) rotational transitions at 551.33 nm. The dye solution used to produce the needed wavelength was prepared by dissolving Fluorescein 548 in methanol at the concentration recommended by the producer Exciton and then adding solid NaOH which usually comes in pellet form until the solution stopped changing color. Quanta Ray dye unit outputs pulses of 0.3 cm^{–1} linewidth and $\approx 5\text{ ns}$ pulse width.

Fluorescence signals were detected at another Suprasil window along a direction at right angles to both laser beams. Signals passed through a system of color filter, lens, low resolution monochromator before being collected by a Thorn Emi 9816QB photomultiplier cooled down to -20°C . The Schott WG 295 color filter cut off the scattering of the ArF laser which could otherwise be revealed to the second and third orders with intensity high enough to be disturbing. A fused silica lens with 38 mm focal length focused the fluorescence on the entrance slit of the Oriel Model 77250 1/8 m monochromator the slit widths of which were set at 1 mm to allow a bandpass of 6.4 nm. Signals were then amplified by a Phillips Scientific Model 6950 preamplifier and a dc coupled Canberra Model 2110 amplifier, and processed by a Tektronics 7912AD transient digitizer. An Olivetti Model M280 computer supervised the data acquisition and the synchronization of the triggering of the lasers, delay generators, and transient digitizer.

To probe the variation of the $v_2''=1$ population with time, it is necessary to fire the dye laser at variable delays with respect to the photolysis flashes. The complexity of the Quanta Ray Nd:YAG laser firing process due to a 3200 μs switching-on time of the Pockels cell, however, makes the realization of such a triggering system with variable delay generation quite complicated. Two homemade delay generators controlled by an external clock were employed and the one producing variable delays was programmable from the computer. The time resolution of our delay generators is 1 μs and the jitter of the dye laser obtainable with our triggering system is approximately $\leq 5\text{ ns}$.

Time-resolved fluorescence signals were recorded triggering the dye laser with a delay of 50 μs with respect to the firing of the photolysis laser in case of quenching data for PH₂(\tilde{A}^2A_1 , $v_2'=1$). Total fluorescence instead was to be collected for reaction data of ground state PH₂ radicals and was obtained by integration via computer of time-resolved signals and stored for each time delay under consideration to give the reaction curve. In both cases, accumulation of a certain number of curves was necessary in order to have statistically tractable data. Kinetic constants could at last be deduced from excited electronic species decay curves or from ground state relaxation curves recorded for various pressures of the collision partners.

Slow flows of the reacting components regulated by a MKS flow control system (MKS Model 147 multigas controller, MKS Model 250 pressure/flow controller provided

with pressure feedback and MKS Model 1259 mass flow meters and flow controllers) prevented accumulation of photolysis products. MKS capacitance manometers were used for pressure monitoring.

PH_3 ($\geq 99.999\%$), Ne ($\geq 99.99\%$), Kr ($\geq 99.998\%$), and Xe ($\geq 99.997\%$) were supplied by Air Liquide while Ar ($\geq 99.9999\%$) and He ($\geq 99.9999\%$) were by Praxair.

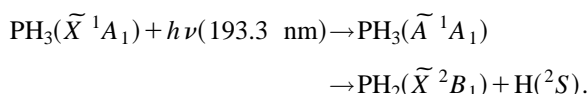
III. RESULTS AND DISCUSSION

In the photolysis of PH_3 by the 193 nm radiation of the ArF laser, we observe fluorescence from the excited electronic species $\text{PH}_2(\tilde{A}^2A_1)$ and $\text{PH}(A^3\pi)$. Sam and Yardley⁶ performed a spectral analysis of this same PH_2 emission and reported a series of vibrational sequences $v'_2-v''_2$ of the $\text{PH}_2(\tilde{A}^2A_1-\tilde{X}^2B_1)$ system with v'_2 up to 8. The spectrum obtained by these authors agreed quite well with those recorded at lower resolution by us in studies of VUV photolysis of PH_3 using a Hanovia hydrogen discharge lamp.^{26,27} These spectra were the first to report fluorescence from $\text{PH}_2(\tilde{A}^2A_1, v'_2 \geq 4)$ as in electrical discharge experiments in PH_3 done by Guenebaut *et al.*²⁸ these emissions were not observed. The assignments for $v'_2 \geq 4$ were thus made exclusively on the basis of absorption data.¹ The same lack of observation of fluorescence from $v'_2 \geq 4$ was also encountered by us in a study of microwave discharges in flowing mixtures of PH_3 with argon²⁹ and was interpreted as due to the fact that in microwave discharges $\text{PH}_2(\tilde{A}^2A_1, v'_2)$ should have been produced by secondary reactions energetically compatible with the formation only of $v'_2 \leq 4$, and not to the onset of a drastic predissociation process; this same argument might also, in our opinion, explain the observations reported in the above mentioned work by Guenebaut *et al.*²⁸ Detection of fluorescence from $v'_2 = 4$ to $v'_2 = 7$ by the LIF technique in our subsequent works³⁻⁵ confirmed definitely the assignments made for the fluorescence spectra produced in the photolysis of PH_3 . $\text{PH}(A^3\pi)$ is instead due to a biphotonic process.

Care thus has to be taken when carrying out laser induced fluorescence on ground state PH_2 radicals to avoid contamination by these spontaneous emissions. The $\text{PH}(A^3\pi-X^3\Sigma^-)$ fluorescence at 342 nm was discriminated by adequate settings of the Oriel monochromator while time discrimination was used for $\text{PH}_2(\tilde{A}^2A_1)$. All the experiments were performed with the monochromator wavelength counter set at 555.5 nm and, as already mentioned, the slit widths opened to 1 mm allowing a transmittance bandwidth of 6.4 nm starting from 552.3 nm. The LIF laser light of 551.33 nm was thus 1.0 nm away from the lower wavelength side of the monochromator transmittance but its scattering was still observed with intensities which however were acceptable for the tractability of the LIF signals themselves. The laser scattering signals could be lowered further down by moving red-wards the counter setting but the LIF signals also decreased so the value of 555.5 nm was chosen as a compromise. As $\text{PH}_2(\tilde{A}^2A_1)$ fluorescence decays in approximately 10 μs for $v'_2 = 0$ which is the level with the

longest lifetime among the v'_2 manifold, the dye laser should be fired with respect to the photolysis laser with a longer delay to be rid of this spontaneous emission.

Sam and Yardley⁶ estimated that $\text{PH}_2(\tilde{A}^2A_1)$ radicals resulted from only $\leq 2\%$ of the dissociation events while Wittig and co-workers^{8,9} reported that the 193.3 nm photolysis of phosphine produced predominantly $\text{PH}_2(\tilde{X}^2B_1)$ with $v'' \geq 3$. Sub-Doppler spectroscopy experiments carried out on the H atom fragment at Lyman- α (121.6 nm) (Refs. 8, 9) allowed the center-of-mass kinetic energy distribution to be extracted and consequently also to obtain the PH_2 internal energy distribution. Since according to this distribution, over half of the PH_2 molecules had internal energies lying below the \tilde{A}^2A_1 origin, it seemed clear that the majority of the PH_2 fragments were formed in the ground electronic state \tilde{X}^2B_1 . The \tilde{X}^2B_1 species production should arise from the reaction



The $\text{PH}_3(\tilde{A}^1A_1)$ equilibrium geometry is almost planar with the HPH angle = 114° while the HPH angle in $\text{PH}_2(\tilde{X}^2B_1)$ is only 91.7° . Thus $\text{PH}_2(\tilde{X}^2B_1)$ should be generated with significant bending excitation on the basis of a simple Franck-Condon argument.

A. Quenching of $\text{PH}_2(\tilde{A}^2A_1, v'_2 = 1)$

As already mentioned, in our previous papers concerning the decay of $\text{PH}_2(\tilde{A}^2A_1)$,^{3,5} the dynamics of various single vibrational levels was investigated under the action of only one collider i.e., the parent molecule PH_3 itself. In this work conversely the time evolution of only one vibrational state $v'_2 = 1$ has been studied under the influence the whole series of rare gases.

$\text{PH}_2(\tilde{A}^2A_1, v'_2 = 1)$ was generated from $(\tilde{X}^2B_1, v'' = 1)$ by laser exciting the rotational transitions $6_{16}-6_{06}$ and $4_{14}-4_{04}$ with the 5513.3 Å wavelength. $(\tilde{X}^2B_1, v'' = 1)$ should be formed by deactivation of $\text{PH}_2(\tilde{A}^2A_1)$ species and by relaxation from higher vibrational levels. Even with the best care we could take in carrying out our experiments, it was not possible to eliminate completely the laser scattering from the $\text{PH}_2(\tilde{A}^2A_1)$ fluorescence signals. Thus in analyzing the time resolved signals the few channels contaminated by laser scattering have not been taken into account.

The $\text{PH}_2(\tilde{A}^2A_1, v'_2 = 1)$ fluorescence decays monoexponentially and follows the well known Stern-Volmer mechanism in all performed experiments,

$$\tau^{-1} = \tau_R^{-1} + \tau_D^{-1} + k_{\text{PH}_3}[\text{PH}_3] + k_M[\text{M}], \quad (1)$$

where τ^{-1} is the signal decay constant, τ_R the $\text{PH}_2(\tilde{A}^2A_1, v'_2 = 1)$ radiative lifetime, τ_D^{-1} the diffusion constant of the excited species out of the viewing zone and negligible with respect to τ_R^{-1} , k_{PH_3} and k_M the quenching rate constants by PH_3 and the added gas M, respectively.

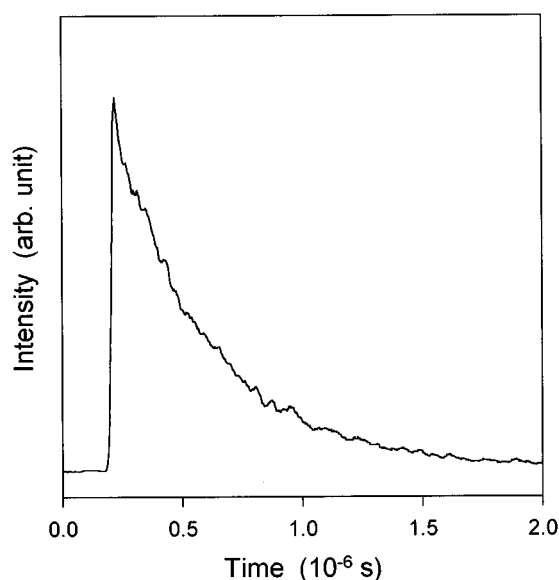


FIG. 1. Time-resolved fluorescence decay of $\text{PH}_2(\tilde{A}^2A_1; 0,1,0)$. 0.1 Torr PH_3 +1 Torr Ar.

In order to have data consistent with each other, care was taken to carry out the experiments the most uniformly possible. Much care also was devoted to the mathematical treatment of the recorded experimental curves. To avoid possible errors introduced by distortions of the baseline due to electromagnetic interferences of the laser discharges and to the initial emissions of $\text{PH}_2(\tilde{A}^2A_1)$ directly produced by photolysis of PH_3 , for each fluorescence curve a blank curve was recorded by firing the ArF laser into the reaction cell while obscuring at the same time the dye laser. As the blank curves did not always coincide with the zero LIF signal line, they were submitted to simple mathematical manipulations to retain only the distortion factors and then subtracted to the fluorescence curves. The fluorescence signals were then referred to a true base line derived from the initial channels of such resulted curves where we were sure that no signals were present. This treatment procedure is described in detail in our previous paper.³

Figure 1 shows the decay of $\text{PH}_2(\tilde{A}^2A_1, v'_2=1)$ in 0.1 Torr PH_3 +1 Torr Ar.

As the pulse width of the probe laser was very short with respect to the fluorescence decay, no deconvolution was necessary.

The signals obtained after the above treatment were fitted to the equation

$$\ln I = -\tau^{-1}t + \ln I_0 \quad (2)$$

by the least-squares method weighted according to photon-counting statistics. The values of τ^{-1} were derived with their external standard deviations.³⁰

τ^{-1} is plotted vs the pressure of various quenchers in Figs. 2 and 3.

For each collision partner, the quenching rate constant k_M was obtained from a least-squares fitting of τ^{-1} weighted

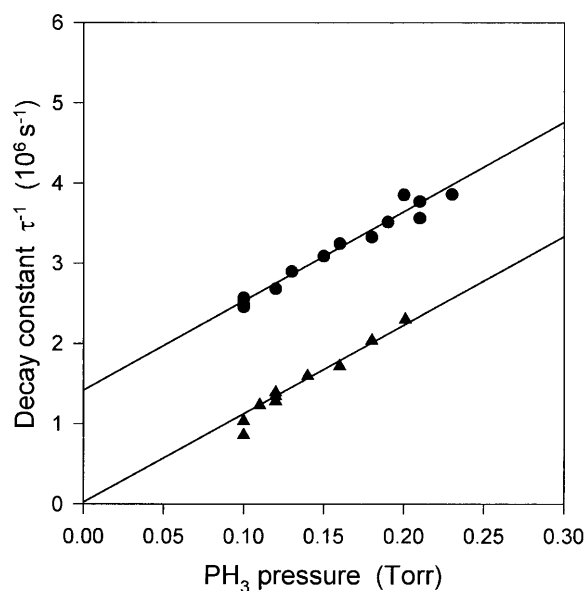


FIG. 2. $\text{PH}_2(\tilde{A}^2A_1; 0,1,0)$ fluorescence decay constant τ^{-1} vs PH_3 pressure. \blacktriangle , static pressure conditions and no buffer gas added; \bullet , flowing mixtures of PH_3 +1 Torr Ar.

by their above-mentioned external standard deviations to Eq. (1). The 95% confidence level error of each k_M thus derived was given by the product of its own external standard deviation and the Student's t factor.³⁰

Table I reports the k_M of the various quenchers, the corresponding cross sections, and their quenching probabilities per collision.

As can be seen, the excellent agreement between the self-quenching constant determined in this work and that re-

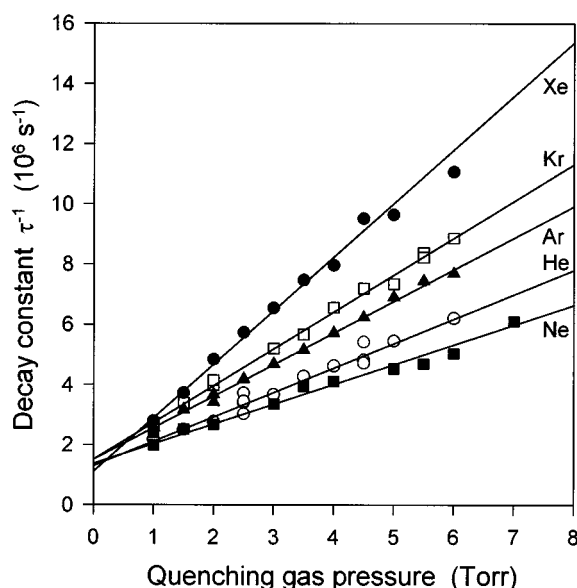


FIG. 3. $\text{PH}_2(\tilde{A}^2A_1; v'_2=1)$ fluorescence decay constant τ^{-1} vs quenching gas pressure. \bullet , Xe; \square , Kr; \blacktriangle , Ar; \circ , He; \blacksquare , Ne. PH_3 pressure, 0.1 Torr.

TABLE I. Quenching of $\text{PH}_2(\tilde{A}^2A_1, v'_2=1)$ by rare gases and PH_3 . Rate constants k_M , cross sections $\langle\sigma\rangle$, and probability per collision P .

Quencher M	$k_M \times 10^{11}$ ($\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$)	$\langle\sigma\rangle$ (\AA^2) ^a	$P = \langle\sigma\rangle / \langle\sigma\rangle_{\text{hs}}$ $\times 10^{2b}$
He	2.51 ± 0.22	1.88 ± 0.17	6.3
Ne	2.03 ± 0.18	2.86 ± 0.25	8.9
Ar	3.24 ± 0.11	5.49 ± 0.18	14.3
Kr	3.78 ± 0.14	7.32 ± 0.27	18.0
Xe	5.50 ± 0.41	11.2 ± 0.8	24.2
PH_3^c	34.1 ± 7.1	55.5 ± 11.6	141
PH_3^d	34.4 ± 3.3	56.0 ± 5.4	142

^aThe quenching cross sections have been derived from k_M according to the formula reported by Yardley in Ref. 37. The room temperature is 298 K.

^bTo calculate the hard sphere collision cross sections σ_{hs} , the diameter of PH_3 has been taken as the average of the diameters of NH_3 and AsH_3 while that of PH_2 has been estimated to be approximately equal to that of H_2S . The diameters of NH_3 , AsH_3 , and H_2S are taken from J. O. Hirschfelder, C. F. Curtiss, and R. Byron Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967). The diameters of the other quenchers are reported in Table II.

^cStatic pressure conditions, and no buffer gas.

^dFlowing mixtures of $\text{PH}_3 + 1$ Torr Ar.

ported in the previous paper³ constitutes a further evidence of the excitation of the $\text{PH}_2(\tilde{A}^2A_1, v'_2=1-\tilde{X}^2B_1, v''_2=1)$ transition by the 551.33 nm laser wavelength.

Various theories have been devised to correlate electronic fluorescence quenching efficiencies with the physical properties of the colliders. According to Rössler,³¹ the quenching constants should be proportional to the product of the polarizability of the quencher α_M and the duration of the collision and thus to $\alpha_M \mu^{1/2}$ where μ is the reduced mass of the collision partners. Selwyn and Steinfeld^{32,33} and Thayer and Yardley^{10,11} based their models on long range interactions and considered transitions between discrete levels and a continuum. The ‘‘Fermi Golden Rule’’ was used for the calculation of the quenching cross sections. Selwyn and Steinfeld found the relationship

$$\sigma(\text{\AA}^2) \propto A \mu^{1/2} I_M \alpha_M / R_c^3, \quad (3)$$

where σ is the cross section, A is a constant which depends on the excited molecule, I_M and α_M are, respectively, the ionization potential and the polarizability of the quencher, R_c is the mean distance of closest approach of the collision pair taken to be the hard-sphere distance $(d_P + d_M)/2$, d_P and d_M being, respectively, the diameters of the excited species and of the quencher.

Thayer and Yardley developed a dipole–dipole interaction model and evaluated the transition matrix element which appears in the Fermi expression using a perturbation expansion. For nonpolar quenchers, the dispersion effect was assumed to be dominant and the following equation was derived:

$$\sigma(\text{\AA}^2) = A \mu^{1/2} I_P^2 I_M^2 (I_P + I_M)^{-2} \alpha_M^2 R_c^{-9} + C, \quad (4)$$

where A and C are constants, I_P is the ionization potential of the excited molecule, while the other parameters have the same meanings as before.

Parmenter and co-workers^{11,12} instead developed a more general theory of collision induced transformation of an excited species A^* to another state B by transferring energy to the surrounding molecules generically termed M ,



Unlike the above-mentioned models which deal specifically with quenching of excited electronic species, Parmenter *et al.*'s theory encompasses a wide range of processes such as the electronic quenching itself, collision induced predissociations, vibrational and rotational relaxations and vibrational stabilization, intersystem crossing, internal conversion, etc. It has been seen to work as well with atomic species as with diatomic, polyatomic molecules, and ions.

The theory assumes the formation in process (5) of some kind of intermediate $[A^*-M]$ the dissociation of which would determine the transformation rate of A^* ,

$$-dA^*/dt = k_d[A^*-M], \quad (6)$$

where k_d is the dissociation constant of the A^*-M pair. The subsequent development follows two different lines. One considering the intermediate simply as a transient interacting pair employs fluid mechanics tools to derive an explicit expression for $-dA^*/dt$ in terms of the densities of A^* and M , k_d and a pair radial distribution function; k_M of Eq. (5) can then be expressed in terms of k_d and this radial distribution function which is directly related to the interaction potential between A^* and M . Mathematical manipulations using different kinds of potentials result in

$$\ln \sigma = \ln C + \beta(\epsilon_{MM}/k)^{1/2}, \quad (7)$$

where σ is the cross section for process (5),

$$\beta = (\epsilon'_{A^*A^*}/kT^2)^{1/2} \quad (8)$$

and

$$(\epsilon_{A^*A^*})^{1/2} = 0.6(\epsilon'_{A^*A^*})^{1/2}. \quad (9)$$

$\epsilon_{A^*A^*}$ and ϵ_{MM} represent the well depths of the A^*-A^* and $M-M$ pair potentials, respectively, and k is the Boltzmann constant.

The other line consists in considering $[A^*-M]$ as in true equilibrium with A^* and M , i.e.,



and thus

$$-dA^*/dt = k_d K[A^*][M],$$

where K is the equilibrium constant. K is then derived from the partition functions and the calculations end up to the same correlation rule.

The transient pair formulation of the theory has outlined the limits of its validity.

- (1) Collision induced processes must be due to interactions dominated by attractive forces;
- (2) Resonance effects between A^* and M must be absent.

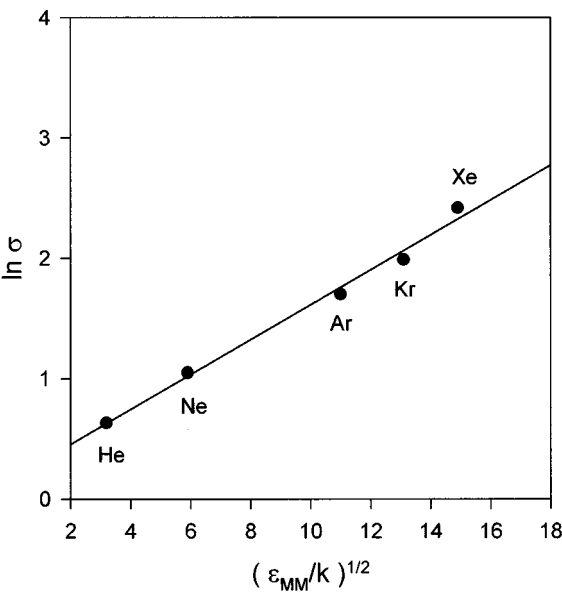


FIG. 4. Parmenter’s plot for the quenching of $\text{PH}_2(\tilde{A}^2A_1; v_2'=1)$ by rare gases. In σ vs $(\epsilon_{\text{MM}}/k)^{1/2}$, σ being the quenching cross section and ϵ_{MM} the intermolecular potential well depth of the quenching gas M.

Apart from the case of self-quenching by the parent molecule PH_3 , our data for the rare gases could not be affected by resonance effects. In Fig. 4, we have plotted $\ln \sigma$ as a function of $(\epsilon_{\text{MM}}/k)^{1/2}$ for the series of rare gas quench-

ers using for $(\epsilon_{\text{MM}}/k)^{1/2}$ the values reported in Table II. As can be seen, the data follow very well the Parmenter and co-workers’ correlation function showing that in the quenching process by rare gases the interactions between $\text{PH}_2(\tilde{A}^2A_1, v_2'=1)$ and the quenchers are dominated by long range attractive forces.

From the slope of Fig. 4, β can be determined and consequently $\epsilon_{\text{PH}_2^*\text{PH}_2}/k$ and $\epsilon_{\text{PH}_2^*\text{M}}/k$ can be computed from Eqs. (8) and (9) and the combination rule $\epsilon_{\text{PH}_2^*\text{M}} \equiv (\epsilon_{\text{PH}_2^*\text{PH}_2} \cdot \epsilon_{\text{MM}})^{1/2}$. These various values are reported in Table II.

We have also tried to correlate our data with the molecular properties of the quenchers and $\text{PH}_2(\tilde{A}^2A_1)$ according to the formula (4) derived by Thayer and Yardley. The plot is displayed in Fig. 5 and a linear correlation is clearly shown. The values of I_{M} and α_{M} for the rare gases are also reported in Table II while the ionization potential of $\text{PH}_2(\tilde{A}^2A_1)$ of 7.55 eV has been calculated as the difference between the ionization potential of ground state PH_2 of 9.824 eV found by Berkowitz *et al.*^{34,35} [$\text{PH}_2 \rightarrow \text{PH}_2^+(\tilde{X}^1A_1) + e$] and the excitation energy $\Delta E(\tilde{A}^2A_1 - \tilde{X}^2B_1) = 2.266$ eV of PH_2 . The same linear correlation is observed even if we take the value of ground state PH_2 ionization potential for I_p in Eq. (4). This correlation confirms the role of long range interactions.

A comprehensive removal mechanism of $\text{PH}_2(\tilde{A}^2A_1)$,

TABLE II. Selected molecular properties^a used for Parameter and co-workers’, and Thayer and Yardley’s plots and well depths of the interaction potentials derived from Figs. 4 and 10.

Quencher M	He	Ne	Ar	Kr	Xe
Diameter $\sigma_{\text{L-J}}$ (Å)	2.6	2.8	3.4	3.6	4.1
Polariz- ability α_{M} (Å ³)	0.204	0.393	1.66	2.48	4.00
Ionization potential I_{M} (eV)	24.6	21.6	15.7	14.0	12.1
ϵ_{MM}/k (K)	10.2	34.8	121.0	171.6	222.0
$\epsilon_{\text{PH}_2^*\text{M}}/k^{\text{b}}$ (K)	82.9	153.0	285.4	339.9	386.6
$\epsilon_{\text{PH}_2^*\text{PH}_2^*}/k$ (K)	673.1				
$\epsilon_{\text{PH}_2-\text{M}}/k^{\text{c}}$ (K)	37.7	69.6	129.8	154.6	175.8
$\epsilon_{\text{PH}_2-\text{PH}_2}/k$ (K)	139.3				

^aThe sources of the molecular property data for He, Ne, Ar, Kr are cited in a previous paper [J. Chem. Phys. **75**, 4912 (1981)]. For Xe, the diameter and polarizability are taken from S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lin, and S. P. Pavlou, J. Phys. Chem. **74**, 3160 (1970); the ionization potential from A. R. Striganov and N. S. Sventitskii, *Tables of Spectral Lines of Neutral and Ionized Atoms* (IFI/Plenum, New York, Washington, 1968). The ϵ_{MM}/k values are all derived from data reported in Ref. 12.

^b PH_2^* represents $\text{PH}_2(\tilde{A}^2A_1, v_2'=1)$.

^c PH_2 represents $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$.

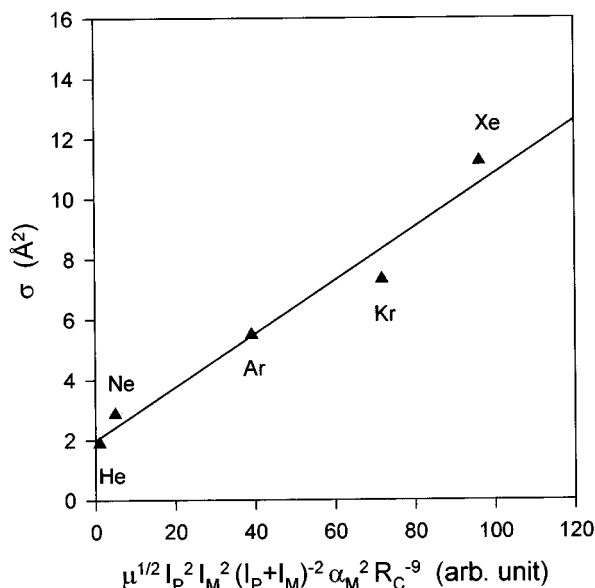


FIG. 5. Thayer and Yardley's plot for the quenching of $\text{PH}_2(\tilde{A}^2A_1; v'_2=1)$ by rare gases.

$v'_2=1$) should include, besides the collision induced electronic transition ($\tilde{A}^2A_1, v'_2=1 \rightarrow \tilde{X}^2B_1, v''_2$), the vibrational relaxation to $v'_2=0$ and the intermode relaxation to the symmetric and antisymmetric stretchings. In our previous paper³ and in some preliminary experiments concerning $v'_2=1$, we have seen that deactivation to lower vibrational levels should not be very efficient while a relaxation through ν_1 and ν_3 seems to be difficult for $v'_2=1$ as the value of $\nu_2=973 \text{ cm}^{-1}$ is far lower than those of $\nu_1=2430$ and $\nu_3=2660 \text{ cm}^{-1}$.⁵⁵ Thus electronic quenching appears to be the main channel for the deactivation of $\text{PH}_2(\tilde{A}^2A_1, v'_2=1)$. This conclusion seems to be supported by the fact that the quenching data are correlated by the Thayer and Yardley's theory which assumes transitions between a discrete level and a continuum constituted here by the high density of states of higher vibrational levels of $\text{PH}_2(\tilde{X}^2B_1)$ underlying $v'_2=1$.

B. Vibrational relaxation of $\text{PH}_2(\tilde{X}^2B_1, v''_2=1)$

Figure 6 represents a time-resolved LIF curve of $\text{PH}_2(v''_2=1)$ at 0.12 Torr PH_3 , recorded with an initial delay of 20 μs from the firing of the photolysis laser, which exhibits clearly a build-up followed by a decay.

A Marquardt–Levenberg nonlinear least-squares fitting weighted according to Poisson statistics was carried out using both equations

$$I = C[\exp(-At) - \exp(-Bt)] \quad (11)$$

and

$$I = C_1 \exp(-At) - C_2 \exp(-Bt), \quad (12)$$

where C , C_1 , and C_2 are pre-exponential constants, and A and B the decay constants. The fitting with Eq. (12) gives equal values for C_1 and C_2 which are themselves equal to

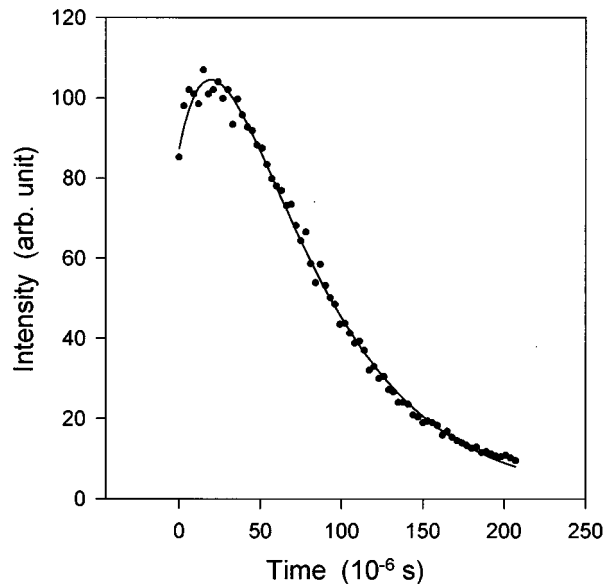


FIG. 6. Time-resolved LIF curve of $\text{PH}_2(\tilde{X}^2B_1; 0,1,0)$. 0.12 Torr PH_3 . Initial delay between the dye laser and the photolysis laser, 20 μs . ●, experimental data. The time interval between successive data points, 3 μs . Fitting to equation $C(-e^{-K_2t} + e^{-K_1t})$ is represented by the continuous line.

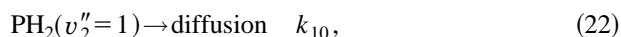
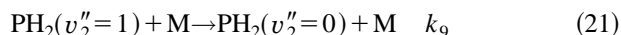
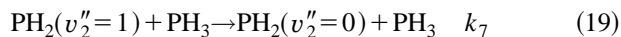
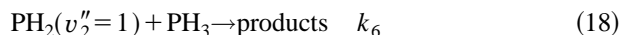
C obtained with Eq. (11). On the other hand the decay constants A and B are also the same from both the above equations with B larger than twice the value of A . It is thus demonstrated that the population evolution of $v''_2=1$ should be on the whole described by Eq. (11).

Equation (11) is typical of a two-level system $|2\rangle$ and $|1\rangle$ coupled with a third ground level $|0\rangle$, where the higher level decays according to a global constant K_2 , and the $|1\rangle$ level having no population at $t=0$ is populated by $|2\rangle$ and decays according to another constant K_1 . The $|1\rangle$ level concentration is described by a function of time of the same form as Eq. (11) with K_1 and K_2 for decay constants.

The fact that $|1\rangle$ is initially unpopulated confirms what was reported by Wittig and co-workers,^{8,9} according to whom the laser photolysis of PH_3 by the 193.33 nm wavelength produces only $\text{PH}_2(\tilde{X}^2B_1, v''_2 \geq 3)$. $v''_2=1$ empty at $t=0$ is populated by cascading from these higher levels. The mechanism involving the time evolution of the $v''_2=1$ population could thus be assimilated to the above-mentioned two-level system where the higher level is constituted by the bulk of the higher vibrational levels produced during the photolysis process and where the lower one is $v''_2=1$.

The kinetic equations assumed to be involved in the time variation of the $v''_2=1$ concentrations after photolysis could thus be





where PH_2^\dagger represents the higher vibrational levels of $\text{PH}_2(\tilde{X}^2B_1)$ and M an added gas. Equation (20) could be omitted in case M is a rare gas.

Actually, $\text{PH}_2(v_2''=1)$ produced from radiative decays or collision induced vibrational relaxation+radiative decays of $\text{PH}_2(\tilde{A}^2A_1, v_2')$ should also be taken into account. But as, according to Sam and Yardley,⁶ the quantum yield of $\text{PH}_2(\tilde{A}^2A_1, v_2')$ should be less than 0.02, the population of $\text{PH}_2(v_2''=1)$ due to radiative processes should be of minor importance.

Let

$$K2 = k_5 + (k_1 + k_2)[\text{PH}_3] + (k_3 + k_4)[\text{M}] \quad (23)$$

and

$$K1 = k_{10} + (k_6 + k_7)[\text{PH}_3] + (k_8 + k_9)[\text{M}]. \quad (24)$$

be the total decay constants of PH_2^\dagger and $\text{PH}_2(v_2''=1)$, respectively.

From the kinetic equations describing the above mechanism, the solution for the $\text{PH}_2(v_2''=1)$ population is derived,

$$[\text{PH}_2(v_2''=1)]_t = [\text{PH}_2^\dagger]_{10} \{ (k_2[\text{PH}_3] + k_4[\text{M}]) / (K2 - K1) \} \times (-e^{-K2t} + e^{-K1t}) \quad (25)$$

which corresponds in fact to Eq. (11).

If $K2 > K1$, the decay portion of the LIF curve should follow the time variation due to e^{-K1t} and gives the decay constant $K1$ of $v_2''=1$ by simple linear least-squares fitting, conversely it should reflect the decay constant $K2$ of PH_2^\dagger .

It is not possible to know *a priori* which one of the two conditions would prevail, but a consideration of the fact that the higher vibrational levels could involve in the deactivation processes more internal degrees of freedom like the stretching modes which could possibly be mixed with the bending one through Fermi resonance or Coriolis couplings, and more intermolecular $V-V, T, R$ or $V-T, R$ channels between PH_2 and the parent molecule PH_3 and the added gases, would suggest to assume that $K2 > K1$.

A more complex kinetic scheme was adopted by Xiang *et al.*³⁶ to describe the relaxation of $\text{NH}_2(\tilde{X}^2B_1, v_2''=1)$ in an experiment where NH_2 was generated in vibrationally excited states $v_2'' > 1$. Such a scheme, which took into account besides the relaxation in the bending mode also the relaxation in the stretching ones and the intermode coupling between the bending and the stretchings at $v_2''=2$, was assumed on the grounds of a LIF curve for $\text{NH}_2(v_2''=1)$ exhibiting nearly equal rise and fall rate constants and which was poorly fitted by single exponentials. The derived coupled master equations gave rise to a very complicated analytical solution for the population of $\text{NH}_2(v_2''=1)$ where more than

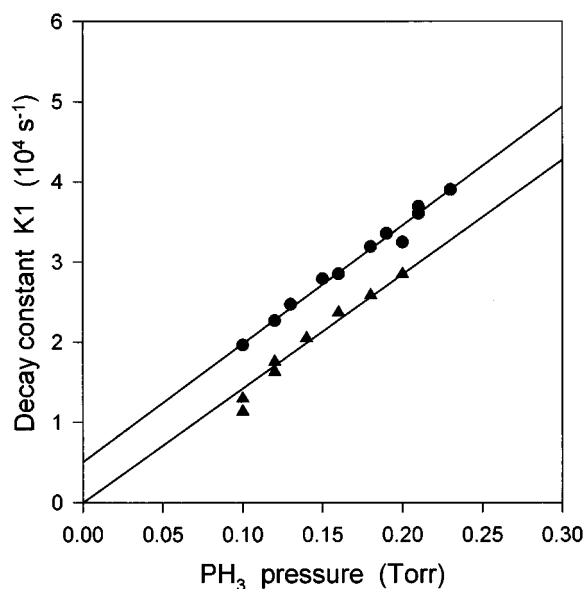


FIG. 7. $\text{PH}_2(\tilde{X}^2B_1; v_2''=1)$ LIF curve decay constant $K1$ vs PH_3 pressure. \blacktriangle , static pressure conditions and no buffer gas added; \bullet , flowing mixtures of $\text{PH}_3 + 1$ Torr Ar.

6 parameters had to be considered. As mentioned previously a similar situation has not been found in this work.

$K1$ were derived mostly by simple fittings of a single exponential function to the decay part of the LIF curves of $\text{PH}_2(v_2''=1)$ as they were in very good agreement with those obtained when nonlinear least-squares fitting of Eq. (25) to the whole curve was carried out.

Since we were interested in obtaining $K1$, only the decay part of the integrated LIF signal curve was recorded in most experiments.

$\text{PH}_2(v_2''=1)$ deactivation study was performed using the whole series of rare gases He, Ne, Ar, Kr, and Xe as quenchers. Measurements of the self-relaxation constant were done both in static pressure conditions and without buffer gas, and in flowing mixtures of PH_3 and 1 Torr Ar. In all experiments with rare gases, 0.1 Torr PH_3 was employed.

While in self-relaxation experiments and in those with He, Ne, Ar, and Kr, the LIF signals decay monoexponentially, in experiments with Xe they rather show a biexponential behavior for which it is not so easy to give a simple interpretation.

Figures 7 and 8 show plots of $K1$ constants vs the quencher pressures.

Table III presents the deactivation constants k_9 for He, Ne, Ar, Kr, and $(k_6 + k_7)$ for self-relaxation in both static pressure conditions and flows, the corresponding cross sections and relaxation probabilities, and for comparison also the quenching constants, cross sections and probabilities of $\text{NH}_2(\tilde{X}^2B_1, v_2''=1)$ reported by Xiang *et al.*²⁴ k_9 and $(k_6 + k_7)$ are represented by k_M in the table.

We have calculated the cross sections and transition probabilities according to the formulas given by Yardley.³⁷

In Fig. 9, the relaxation probabilities of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ are plotted vs $\mu^{1/2}$ with μ representing the reduced

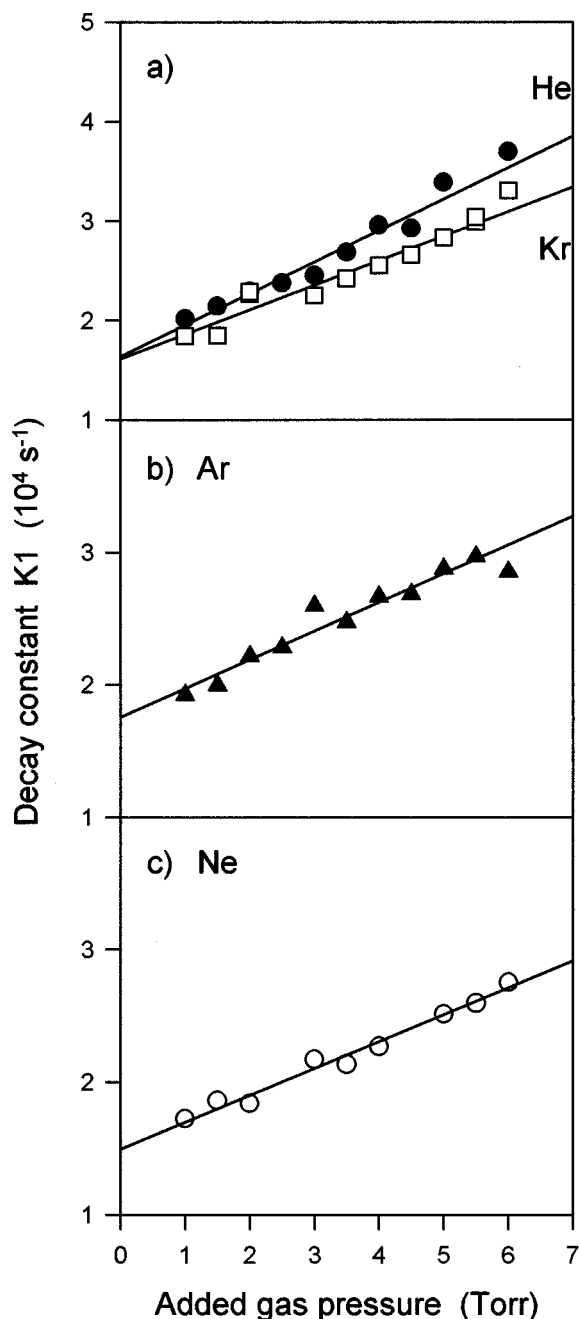


FIG. 8. $\text{PH}_2(\tilde{X}^2B_1; v_2''=1)$ LIF curve decay constant K_1 vs added gas pressure. (a) \bullet , He; \square , Kr. (b) Ar. (c) Ne. PH_3 pressure, 0.1 Torr.

mass of PH_2 and its rare gas collision partners.

The quenching constants and the corresponding probabilities are higher for NH_2 by an average factor of 3.9. But as can be seen, there is somewhat a kind of parallelism between PH_2 and NH_2 for what concerns the variation trend of the relaxation probability with the reduced mass of the collision pair, even if a difference exists for He.

In NH_2 the probability for the quenching of $v_2''=1$ decreases from He to Ne then increases from Ne to Kr while that of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ increases monotonically from He to Kr.

Vibrational relaxation data of polyatomic molecules should be interpreted by the extensions due to Tanczos³⁸ and Stretton³⁹ of the SSH theory of $V-T$ energy transfer originally formulated for diatomic molecules,²⁵

$$P_{i-f} = P_0 g_f |U_{i-f}|^2 I(\Delta E, T, \mu, \alpha, \epsilon), \quad (26)$$

where P_{i-f} is the transition probability from state i to state f , P_0 a steric factor, g_f the final state degeneracy, $|U_{i-f}|^2$ the square of the vibrational transition moment. $I(\Delta E, T, \mu, \alpha, \epsilon)$ depends on the amount of energy ΔE to be transferred from vibration to translation, the temperature T , the reduced mass of the collision pair μ , the intermolecular repulsion parameter α , and the Lennard-Jones well depth ϵ , and can be considered as a translational factor which reflects changes in the transition probability through ΔE and the relative velocity (T, μ, ϵ) . If the initial and final states are the same for all collision induced transitions, I should represent the relative probability of energy transfer.

Flynn and Ronn with their co-workers⁴⁰⁻⁴⁶ have carried out the calculations of $I(\Delta E, T, \mu, \alpha, \epsilon)$ by numerical integration, for different values of the parameters on which it depends, i.e., ΔE , μ , α , etc., and for a certain number of polyatomic systems, and have found that the transfer probabilities increase with $\mu^{1/2}$ for small ΔE while its \ln values decrease approximately linearly with $\mu^{1/2}$ for $\Delta E \geq 1000 \text{ cm}^{-1}$ with the transition point at $\sim 200 \text{ cm}^{-1}$.

The SSH-Tanczos equation has been seen to be able to explain qualitatively the variation trend of energy transfer efficiency with $\mu^{1/2}$ for collision induced $V-V$ processes where the energy defects are small⁴¹ but cannot account for $V-T$ deactivations reported for a series of methyl halides where the relaxation probabilities are not very sensitive to the reduced mass in the rare gas quenchers series.⁴³⁻⁴⁶ From Fig. 9, it is also evident that the relaxation behavior of $\text{PH}_2(v_2''=1)$ with $\Delta E = \nu_2 = 1102 \text{ cm}^{-1}$ does not follow the SSH-Tanczos theory. In the case of $\text{NH}_2(v_2''=1)$, SSH-Tanczos seems to be obeyed from He to Ne but then the situation becomes similar to that of $\text{PH}_2(v_2''=1)$ for heavier quenchers.

In trying to find out the reason for which some deuterated molecules relax more slowly than the corresponding hydrogenated compounds in spite of the fact that their vibrational frequencies are smaller, Cottrell⁴⁷⁻⁴⁹ suggested for the first time that since the rotational velocity of the hydrogen atoms is larger than the molecular translational velocity, the vibrational energy transfer into rotation might be more probable than into translation. Following the same idea, Moore⁵⁰ derived an equation for vibration-rotation energy transfer by simple substitution of ωd and I/d^2 , respectively, to the translational relative velocity and the reduced mass in the equation by Cottrell and McCoubrey⁵¹ for vibration-translation energy transfer, ω and I being, respectively, the angular frequency and the moment of inertia of the rotator and d the distance of the peripheral atoms from its center of mass. The formula obtained, albeit derived from a simple model, succeeded in correlating data where interpretation in terms of $V-T$ transfer was unsuccessful and showed that for

TABLE III. Collision-induced vibrational relaxation of $\text{PH}_2(\tilde{X}^2B_1; 0,1,0)$ and $\text{NH}_2(\tilde{X}^2B_1; 0,1,0)$. Rate constants k_M , cross sections $\langle\sigma\rangle$,^a and probabilities per collision P .

Quencher M	PH_2			NH_2^b		
	$k_M \times 10^{14}{}^c$ ($\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$)	$\langle\sigma\rangle \times 10^3$ (\AA^2)	$P = \langle\sigma\rangle / \langle\sigma\rangle_{\text{hs}}$ $\times 10^4{}^d$	$k_M \times 10^{13}$ ($\text{cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$)	$\langle\sigma\rangle \times 10^2$ (\AA^2)	P $\times 10^3$
He	9.77 ± 1.66	7.34 ± 1.24	2.44	3.41 ± 0.03	2.43 ± 0.02	0.99
Ne	6.26 ± 0.70	8.82 ± 0.99	2.75	1.75 ± 0.99	2.08 ± 1.18	0.80
Ar	6.70 ± 1.37	11.3 ± 2.3	2.95	3.03 ± 0.08	4.08 ± 0.11	1.26
Kr	7.65 ± 1.71	14.8 ± 3.3	3.65	3.58 ± 0.06	5.22 ± 0.09	1.52
PH_3^e	440 ± 19	716 ± 31	181			
PH_3^f	456 ± 37	743 ± 60	188			

^aThe cross sections have been calculated from k_M according to the formula given in Ref. 37. The room temperature is 298 K.

^bThe values for k_M and P are taken from Ref. 24 while $\langle\sigma\rangle$ have been derived by us from k_M .

^c k_M represents k_9 for rare gas quenchers and $(k_6 + k_7)$ for self-relaxation. These constants have been derived with 95% confidence level errors from weighted least-squares fittings of $K1$ to Eq. (24). $K1$ were obtained from fittings weighted according to Poisson statistics.

^dThe hard sphere cross sections $\langle\sigma\rangle_{\text{hs}}$ have been considered as equal to those calculated for the quenching of $\text{PH}_2(\tilde{A}^2A_1)$.

^eStatic pressure conditions, and no buffer gas.

^fFlowing mixtures of $\text{PH}_3 + 1$ Torr Ar.

hydrogen or deuterium atom containing compounds the vibrational relaxation due to a $V-R$ process might prevail over $V-T$.

One direct consequence of the neglect of the relative translational velocity in Moore's theory is the fact that the energy transfer efficiency should not be very sensitive to the reduced mass of the system, and this, according to Ronn and co-workers,⁴⁵ would explain in the heavier members of the methyl halide series the deviation from the SSH theory of the dependence of the vibrational deactivation probabilities, originally attributed to $V-T$ processes, upon the mass of the rare gas quenchers.

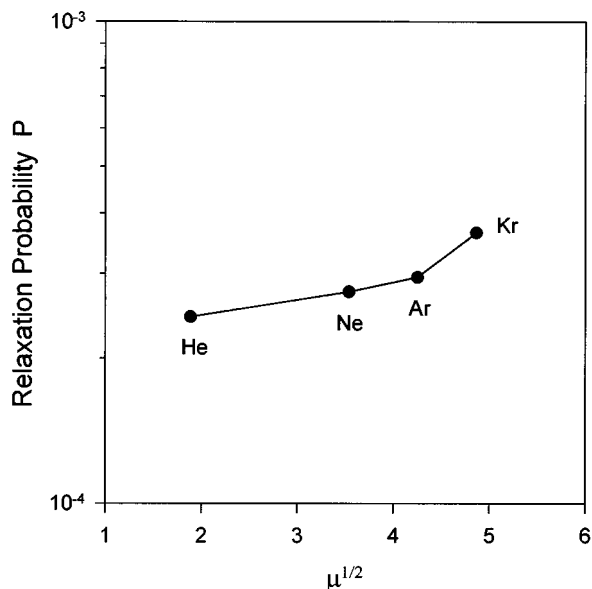


FIG. 9. Collision-induced relaxation probability P of $\text{PH}_2(\tilde{X}^2B_1; v_2''=1)$ vs square root of the reduced mass μ of the collision pair, $\text{PH}_2(v_2''=1) + \text{M}$.

Miklavc and Fischer have proposed more sophisticated semiclassical and quantum mechanical theories, the so-called “effective mass theories” of collision induced vibrational-rotational transitions^{52–54} in which, unlike Moore's theory, translation is taken into account. They have been able to calculate the relaxation probabilities of the methyl halides due to rare gases which agree very well with experimental data^{41,43,44,45} confirming the earlier interpretations by Ronn *et al.* and the predominant role that rotation can play in the vibrational deactivation of molecules having small moments of inertia.

At first sight, only a vibration-translation energy transfer process could be expected for the deactivation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ by rare gas quenchers, as an intramolecular $V-V$ transfer would be impracticable due to large energy defects between $\nu_2 (= 1102 \text{ cm}^{-1})$ and the stretching modes $\nu_1 = 2330$ and $\nu_3 = 2495 \text{ cm}^{-1}$.⁵⁵ The dependence of the deactivation probabilities upon the quencher mass however deviates definitely from the SSH theory, and in the light of what has just been illustrated above, $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ should be deactivated not by a pure $V-T$ but instead by a predominant intramolecular vibration-rotation energy transfer process. This should not be quite surprising as the parent molecule PH_3 belongs to the class of molecules the vibrational relaxation times of which are fit by the Moore's simple vibration-rotation theory.⁵⁰

Xiang *et al.*²⁴ also have invoked the $V-R$ process as the dominant deactivation channel for $\text{NH}_2(\tilde{X}^2B_1, v_2''=1)$ to explain the non-SSH dependence of its transition probability upon the different rare gas quenchers.

On the other hand, in the comparison of the collision-induced relaxation efficiencies of $\text{PH}_2(v_2''=1)$ with those of $\text{NH}_2(v_2''=1)$, a $V-R$ process would explain also the lower values found in PH_2 which has a vibrational frequency $\nu_2 = 1102 \text{ cm}^{-1}$ quite smaller than the $\nu_2 = 1497 \text{ cm}^{-1}$ of

NH_2 . In fact, in a $V-R$ transfer the lower moments of inertia of NH_2 would more than compensate its unfavorable energetic factor which otherwise would be determinant if a $V-T$ process is predominant. The larger reduced mass of PH_2 -collider pairs might in part be responsible for these lower relaxation probabilities but could not in our opinion justify a factor of 3–4 lower.

In a $V-R, T$ process it is not easy to quantify the contribution of the translational channel in deactivating the vibrational energy. According to Miklavc and Fischer,⁵² the leveling off of the relaxation probabilities in methyl halides with respect to the heavier quenchers is indicative of the fact that most of the available energy goes into rotation.

Conversely to the other members of the methyl halide series for which the relaxation probabilities do not vary very much with the nature of the rare gas quenchers, the transition probability of CH_3F exhibits a steep fall with the increase in the reduced mass of the collision pair. This is due, according to Miklavc and Fischer, to very weak long range attractive forces between the collision partners. This steep fall is also shown clearly in the calculations by Miklavc and Smith⁵⁶ for the deactivation of C_2D_2 by the rare gases when the well depth of the interaction potential is chosen to be equal to zero. The long range forces thus should play a non-negligible role in the $V-R$ transfer.

The self-quenching constants have been determined in two types of experiments, one using pure PH_3 without buffer gas in static pressure conditions and the other operating with flowing mixtures of PH_3 and 1 Torr of argon. The agreement between the constants thus obtained is very good and shows that flow experiments would prevent accumulations of photolysis products but could be not strictly necessary to get good results. Xiang *et al.*²⁴ in their IR-MPD experiments operated in static pressure conditions. The self-quenching constant is almost two orders of magnitude larger than the quenching constants measured for the rare gases and could easily be understood on the grounds of the greater number of degrees of freedom of PH_3 which should allow more possible channels for energy transfer including the reactive ones.

While the behavior of xenon appears to be normal, i.e., similar to those of the other rare gases, in the quenching of $\text{PH}_2(\tilde{A}^2A_1)$, it is not easy to explain in the relaxation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$. Xenon is known⁵⁷ to be ionized by the 193.3 nm laser wavelength in a two-photon process and Xe^+ could have somehow interacted with PH_3 and interfered with the formation of vibrationally excited species of $\text{PH}_2(\tilde{X}^2B_1)$ due originally only to the photolysis of PH_3 . Further investigations are being carried out in order to get some insight into this problem.

According to Parmenter and co-workers,¹² processes with cross sections orders of magnitude below hard sphere values should rely on repulsive forces and should not be expected to fit their correlation formula. The cases of vibrational relaxation in the ground state of BCl_3 , C_2H_4 , and CHCl_3 have been produced as evidence.

In spite of the very low values of the relaxation cross sections found for $\text{PH}_2(v_2''=1)$ which are about 3×10^{-4}

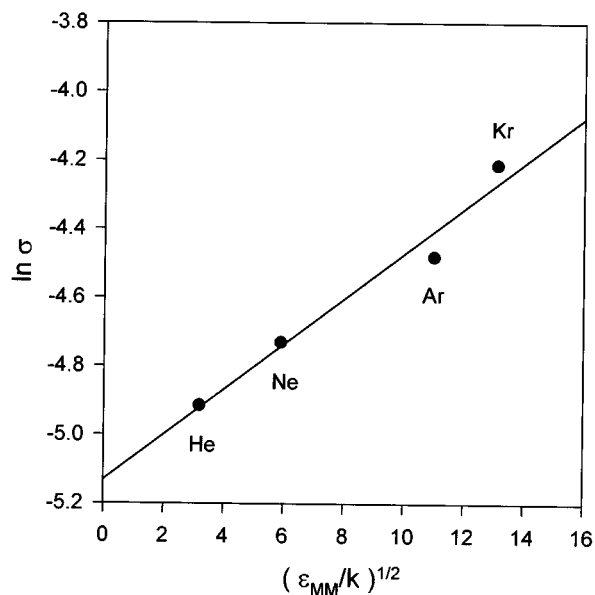


FIG. 10. Parmenter's plot for the relaxation of $\text{PH}_2(v_2''=1)$ by rare gases.

times the hard sphere cross sections, we have tried to plot these data according to the Parmenter *et al.*'s equation (7). The result is shown in Fig. 10. As can be seen, the data seem to follow quite well the theory. According to Parmenter and co-workers,^{12,13} the correlation is a sensitive test for the types of forces which control the interactions or more specifically the "correlation works for attractive forces and fails when repulsive forces become important." We are thus, for the collision induced vibrational relaxation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ by rare gases, in the presence of operating long range attractive forces.

From the slope of Fig. 10 we have also deduced β and then $\epsilon_{\text{PH}_2-\text{PH}_2}/k$ and $\epsilon_{\text{PH}_2-\text{M}}/k$. These values also are reported in Table II.

The relaxation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ by rare gases, as discussed above, should be due predominantly to vibration-rotation energy transfer. The arguments are based on Moore's theory and the calculations done for the relaxation of methyl halides with the "effective mass theory" by Miklavc and Fischer. Both these theories are derived using a repulsive exponential potential. The long range interaction evidenced in Fig. 10 should not however contradict Moore's, and Miklavc *et al.*'s theories as both of them contemplate the contribution of attractive forces in the transfer efficiency. What is striking, instead, is the fact that the Parmenter's plot seems to suggest a predominance of long range forces in the $V-R$ process for the deactivation of $\text{PH}_2(v_2''=1)$.

Usually the long range forces are assumed for near-resonant processes like in the Sharma-Brau theory.^{58,59} It has however been shown that, in many far-from-resonance $V-V$ energy transfer processes like those involving the ground electronic state $v=1$ vibrational level of CO, NO or the hydrogen halides HX and the quenchers CO_2 , NO_2 , etc., the multipolar attractive forces play an important role.⁶⁰⁻⁶³ In hydrogen halides, the vibrational energy discrepancy should,

by the same reason as above of the rotational velocity of the H atom being larger than the relative velocity of the colliding pair, predominantly be transferred into the rotation of HX where rotational multiquantum jumps are considered.

While the importance of long range forces in far-from-resonance $V-V, R, T$ processes has been demonstrated by Seoudi *et al.*^{62,63} and Dillon *et al.*^{60,61} through calculations, the role played by these forces in the $V-R$ deactivation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ has been shown indirectly by the Parmenter and co-workers' theory.

The well depth of the interaction potential between the excited species $\text{PH}_2(\tilde{A}^2A_1, v_2'=1)$ is larger by a factor 4.8 than that between the ground state species $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$. It is reported that generally the excited state well depths are more than two times the values found in the ground state,¹³ and a factor of 5 is encountered in another triatomic molecule SO_2 and in $\text{I}_2(B^3\pi_0, v'=15)$. The large difference between the measured cross sections for the deactivation of $\text{PH}_2(\tilde{A}^2A_1, v_2'=1)$ and $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$, more than two orders of magnitude, can be related, besides to the different nature of the processes respectively involved, also somehow to this large difference in the potential well depths.

Experiments will be performed in conditions where ionization of Xe should be less likely to occur, like for example photolysis of $\text{PH}_3 + \text{Xe}$ by KrF or XeCl laser wavelengths, in order to check the possibility of a determination of the $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ relaxation constant by xenon.

We have also tried to represent the relaxation cross sections of $\text{NH}_2(\tilde{X}^2B_1, v_2''=1)$ measured by Xiang *et al.*²⁴ in a Parmenter's plot. For the rare gas quenchers, Ne, Ar, and Kr lie right on a straight line while He is left out. Thus, for the heavier rare gases long range interactions seem to be predominant. From the slope, we have derived $\epsilon_{\text{NH}_2-\text{NH}_2}/k = 527.9$ K larger than $\epsilon_{\text{PH}_2-\text{PH}_2}/k$ by a factor 3.8, which is reasonable considering that the dipole moment of NH_3 (1.47 D) is 2.5 times that of PH_3 (0.58 D). We have also calculated $\epsilon_{\text{NH}_2-\text{Ne}}/k = 135.5$, $\epsilon_{\text{NH}_2-\text{Ar}}/k = 252.7$ and $\epsilon_{\text{NH}_2-\text{Kr}}/k = 301.0$ K. For H_2 , D_2 , O_2 , N_2 , and CO there seems to be a correlation between He, D_2 , and N_2 which would stay on another line having the same slope as that of the heavier rare gases, but this might be fortuitous as the energy transfer mechanisms might not be the same for all these three quenchers. O_2 should give rise to a near resonant $V-V$ transfer and thus should not be considered. The fact that all the quenchers considered could possibly not be correlated by a single Parmenter's plot in case of predominance of long range forces should be due to involvement of processes of different nature.

IV. CONCLUSION

Quenching of $\text{PH}_2(\tilde{A}^2A_1, v_2'=1)$ has been investigated for the whole series of rare gases. The cross sections behave according to the potential well depth correlation rule and the

interactions should operate under the attractive forces. The quenching data are also well correlated by Thayer and Yardley's theory.

The collision induced vibrational relaxation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ by He, Ne, Ar, and Kr parallels somewhat that of the corresponding species in NH_2 . The deactivation probabilities do not follow the variation trend vs the reduced masses prescribed by the SSH-Tanczos theory in case of a pure $V-T$ transfer. Such a non-SSH behavior has also been observed in the vibrational relaxation of a certain number of polyatomic molecules in the ground electronic state and an energy transfer dominated by an intramolecular $V-R$ process has been invoked. The deactivation cross sections of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$, besides, fit quite well the Parmenter and co-workers' correlation showing that the interactions of these ground electronic state radicals with the rare gas colliders are also governed by long range attractive forces. Xenon has instead been seen to interact in a peculiar way with $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ denoting the onset of some different chemical processes due probably to ionization of this rare gas by the 193 nm laser radiation.

Extension of the investigations to more complex collision partners will be carried out. It should also be useful, if possible, to perform calculations on the deactivation of $\text{PH}_2(\tilde{X}^2B_1, v_2''=1)$ to verify in a more quantitative way both the nature of the energy transfer processes involved and that of the interaction forces.

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