

THE REACTION OF $\text{Pb}(6^3\text{P}_0)$ WITH N_2O AT ELEVATED TEMPERATURES STUDIED BY TIME-RESOLVED ATOMIC RESONANCE ABSORPTION SPECTROSCOPY

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Summary

We present the first direct kinetic study of the reaction $\text{Pb} + \text{N}_2\text{O} \rightarrow \text{PbO} + \text{N}_2$, by time-resolved atomic resonance absorption spectroscopy. $\text{Pb}(6^3\text{P}_0)$ was generated by the low energy pulsed irradiation of PbBr_2 vapour in equilibrium with its solid at elevated temperatures and monitored in the "single-shot mode" by attenuation of the resonance transition at $\lambda = 283.3 \text{ nm}$ ($\text{Pb}(7^3\text{P}_1^o) \leftarrow \text{Pb}(6^3\text{P}_0)$). Absolute second-order rate constants for the process ($k_{\text{N}_2\text{O}}$) were measured across the temperature range 648 - 783 K yielding the Arrhenius form

$$k_{\text{N}_2\text{O}} = 6 \times 10^{-11} \exp\left(\frac{-68 \pm 10 \text{ kJ mol}^{-1}}{RT}\right) \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

(error 1σ in E_{act}). There is an uncertainty of a factor of about 2 in the Arrhenius A parameter. This measurement is compared with analogous data for other group IV atoms in their ^3P ground states, including Arrhenius parameters for the processes $\text{Sn}(5^3\text{P}_0) + \text{N}_2\text{O}$ and $\text{Ge}(4^3\text{P}_j) + \text{N}_2\text{O}$ derived from time-resolved resonance absorption spectroscopy and high temperature fast flow reactor measurements. Single temperature rate data for $\text{C}(2^3\text{P}_j)$ and $\text{Si}(3^3\text{P}_j)$ with N_2O are also considered. Finally, the feasibility of observing chemiluminescence via the $a \rightarrow X$ and $b \rightarrow X$ systems of PbO from $\text{Pb} + \text{N}_2\text{O}$ is discussed.

1. Introduction

The class of oxygen-atom abstraction reactions from the linear 16-electron molecule N_2O [1] by other atoms is of general interest for a number of fundamental reasons. Whilst the bond dissociation energy of this molecule is relatively low ($D(\text{N}_2\text{—O}) = 1.667 \text{ eV}$ [2]) and atomic abstraction is consequently exothermic, electron promotion in N_2O during reaction leads

to large energy barriers. Consequently, rate processes are often slow despite correlation between reactant and product states on the basis of either weak spin-orbit coupling [3, 4] or J, Ω coupling [5]. Once reaction takes place, electronically excited states of the product diatomic oxide molecules become energetically accessible and chemiluminescence is often observed [6]. The reaction of metal atoms with N_2O is generally slow and is usually amenable to study only at high temperatures [6] where N_2O itself is fortunately stable [7] within the time scales of many such measurements. These two latter kinetic properties have led to the frequent use of bimolecular processes involving N_2O as kinetic standards for high temperature metal-atom reactions such as, for example, the recent study of $Na + N_2O$ reported by Husain and Marshall [8]. Despite a long practical interest in the reactions of lead atoms at elevated temperatures, arising from the use of $Pb(C_2H_5)_4$ in "antiknock" for the internal combustion engine, it is only recently that a technique has been developed to characterize rate constants for reactions of atomic lead directly and absolutely at high temperatures [9]. This method of time-resolved atomic resonance absorption spectroscopic monitoring of ground state lead atoms, $Pb(6^3P_0)$, following pulsed irradiation of a lead halide vapour at elevated temperature, is now applied to the kinetic study of $Pb + N_2O$.

The absolute rate constant for the reaction $Sn(5^3P_0) + N_2O$ has been characterized as a function of temperature by both time-resolved atomic absorption spectroscopy following flash photolysis (FPAS) [10, 11] and the use of atomic resonance absorption and molecular chemiluminescence in a high temperature fast flow reactor (HTFFR) [6, 12, 13]. The specific reactivity of the individual three close lying spin-orbit states in $Ge(4^3P_{0,1,2})$ [14] with N_2O have been characterized by similar techniques (FPAS [15, 16]; HTFFR [6, 17]). Swearingen *et al.* [18] have reported the rate constant for the reaction $Ge(4^3P_0) + N_2O$ at a single temperature (300 K) in a flow discharge system using atomic absorption spectroscopy. For the lighter elements carbon and silicon where the closely spaced spin-orbit levels are in Boltzmann equilibrium throughout reaction, Husain and coworkers have reported absolute rate data for $Si(3^3P_J) + N_2O$ [19] and $C(2^3P_J) + N_2O$ [20, 21]. However, these measurements, carried out by time-resolved atomic resonance absorption spectroscopy in the vacuum UV, were necessarily restricted to single temperatures for these very fast processes [19-21]. Until our recent measurements using $PbBr_2$ vapour as the photochemical precursor for lead, rate data for $Pb(6^3P_0)$ derived from the FPAS technique were principally restricted to room temperature measurements because of the thermal decomposition of the precursor previously employed, $Pb(C_2H_5)_4$. Thus, Husain and Littler [22] have reported a limit for $k(Pb + N_2O, T = 300 \text{ K})$ which is of a magnitude typical for that type of experimental system and merely indicates that measurement of the rate process was outside the range of the technique. At the elevated temperatures employed here, the reaction between $Pb + N_2O$, whilst exhibiting a large activation energy, becomes sufficiently rapid to be characterized as described in this paper.

2. Experimental details

The experimental arrangement has been described in detail hitherto [9] and is only briefly summarized here. The reaction was investigated using an electrically heated Spectrosil quartz cylindrical reactor which had independently heated evacuated end compartments to prevent condensation on the end windows and to maintain a constant temperature along the length of the reactor. $\text{Pb}(6^3\text{P}_0)$ was generated in the reactor by the low energy ($E \approx 16 \text{ J}$; $2 \mu\text{F}$; about 4 kV) flash photolysis of PbBr_2 vapour in equilibrium with the solid [23, 24], in the temperature range $648 - 783 \text{ K}$. Entry of gases into the reactor was controlled by means of a magnetic plug [25]. $\text{Pb}(6^3\text{P}_0)$ in the presence of N_2O was then monitored in the "single-shot mode" by time-resolved atomic resonance absorption spectroscopy at $\lambda = 283.3 \text{ nm}$ ($\text{Pb}\{7s(^3\text{P}_1^o)\} \leftarrow \text{Pb}\{6p^2(^3\text{P}_0)\}$, $gA = 1.8 \times 10^8 \text{ s}^{-1}$ [26]). The limited resolution of the small monochromator employed for optical isolation of the atomic transition (Grubb Parsons M2 monochromator) permitted the use of the Beer-Lambert law for the absorption of the atomic radiation, as described previously [9]. The resonance source comprised a high spectral output hollow cathode lamp (Westinghouse, U.S.A., 7 mA , 1000 V), monitored photoelectrically (EMI 9783B photomultiplier tube). The resulting signals were then amplified without distortion [27], captured, digitized and stored in a transient recorder (Data Laboratories DL 905) operating in the "A/B" mode in order to monitor the attenuated and unattenuated signals on different time scales. The data was then transferred to paper tape (Data Dynamics Punch 1183) for subsequent analysis on the University of Cambridge IBM 3081 computer, following the procedure outlined by Clark and Husain [28, 29]. This employs the combination of the Beer-Lambert law with the assumption of an overall first-order decay for $\text{Pb}(6^3\text{P}_0)$, in this case, to fit the resulting digitized data to the form

$$I_{\text{tr}} = I_0 \exp\{-A \exp(-k't)\} \quad (1)$$

where I_{tr} is the attenuated signal, I_0 is the unattenuated signal, A is a constant and k' is the overall first-order decay coefficient for the removal of $\text{Pb}(6^3\text{P}_0)$ — the object of kinetic interest. All materials were prepared as described previously [8, 9].

3. Results and discussion

Figure 1(a) gives an example of the decay of $\text{Pb}(6^3\text{P}_0)$ following the pulsed irradiation of PbBr_2 in the presence of helium alone, in the form of the digitized time variation of the transmitted light intensity at $\lambda = 283.3 \text{ nm}$. The resonance absorption signal was analysed for the region BC (Fig. 1(a)) for the time-dependent component of I_{tr} where, for degrees of light absorption of less than about 50%, the Beer-Lambert law may be employed and data fitted to eqn. (1). The resulting value of k' ($166 \pm 37 \text{ s}^{-1}$) is consistent

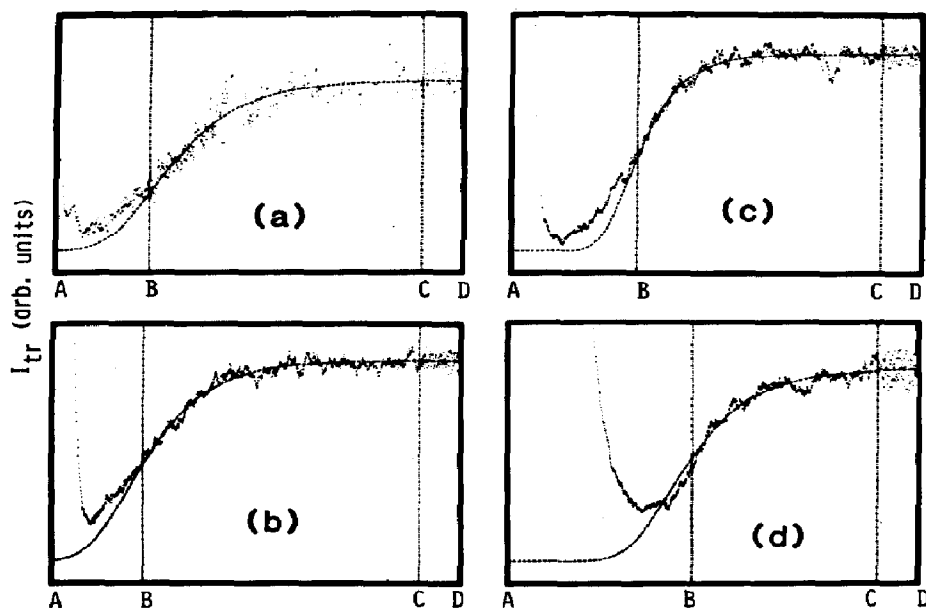


Fig. 1. Examples of the digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 283.3$ nm ($\text{Pb}\{7s(3^1P_1)\} \rightarrow \text{Pb}\{6p^2(3^1P_0)\}$) indicating the decay of resonance absorption by ground state lead atoms following the pulsed irradiation of PbBr_2 vapour in the presence of N_2O : $E = 16$ J; abscissa labelling indicates the time base of the transient recorder (AC, A sweep; CD, B sweep; BC, portion of the A sweep analysed for the kinetic decay of $\text{Pb}(6^3P_0)$); dots, data points, ---, computerized fitting to the form $I_{tr} = I_0 \exp\{-A \exp(-k't)\}$; I_0 , arbitrary units; k' , pseudo-first-order rate coefficient for the decay of $\text{Pb}(6^3P_0)$.

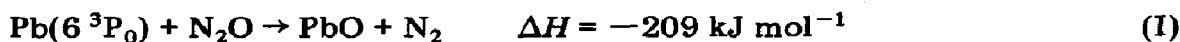
	T (K)	$[\text{He}]$ ($\times 10^{17}$ atoms cm^{-3})	$[\text{N}_2\text{O}]$ (molecules cm^{-3})	AC (ms)	CD (s)
(a)	718	9.7	0	46.2	1
(b)	667	0	9.3	18.48	1
(c)	719	0	9.5	18.48	1
(d)	783	0	9.4	4.62	1

with the loss of $\text{Pb}(6^3P_0)$ by diffusion to the walls of the reactor using our previously reported measurement of the diffusion coefficient, $D_{12}\{\text{Pb}(6^3P_0)\text{-He}\} = 0.48 \pm 0.03$ $\text{cm}^2 \text{s}^{-1}$ at s.t.p. [9], the "long time" solution of the diffusion equation for a cylinder [30, 31] and a $T^{3/2}$ temperature dependence of the diffusion coefficient. In view of the relatively slow rate of removal of $\text{Pb}(6^3P_0)$ by N_2O even at elevated temperatures (see below), the contribution to the overall loss by chemical reaction alone cannot be studied in isolation but must be included in an analysis that represents the combination of both this process and diffusional loss to the walls. Large concentrations of N_2O must be used in order to yield a first-order decay coefficient for removal by chemical reaction which is significant by comparison with that for diffusion. Indeed, pure N_2O must be used in practice. Figures 1(b) and 1(c) show examples of the decay of $\text{Pb}(6^3P_0)$ in the presence of N_2O at pressures

approximately equal to that of helium in Fig. 1(a), at different temperatures, where diffusional loss will be comparable. Thus the effect of chemical reaction of $\text{Pb}(6^3\text{P}_0)$ is apparent. The extent of light absorption by N_2O itself at these low flash energies is small [32]. The pseudo-first-order decay coefficient k' derived from decay traces of the type given in Figs. 1(b) - 1(d) may thus be represented by two terms:

$$k' = \frac{\beta}{p_{\text{N}_2\text{O}}} + k_{\text{N}_2\text{O}} p_{\text{N}_2\text{O}} \quad (2)$$

where $k_{\text{N}_2\text{O}}$ represents the absolute second-order rate constant for the reaction



($D_0^{\circ}\{\text{PbO}(X^1\Sigma^+)\} = 3.83 \text{ eV}$ [32]) in the appropriate units of pressure and, for a cylindrical reaction vessel

$$\beta \approx \frac{5.81 D'_{12}}{r^2} \quad (3)$$

where $D'_{12} \equiv D\{\text{Pb}(6^3\text{P}_0)\text{-N}_2\text{O}\}$. As $k_{\text{N}_2\text{O}}$ is the required quantity, eqn. (2) is recast in the form

$$k' p_{\text{N}_2\text{O}} = \beta + k_{\text{N}_2\text{O}} p_{\text{N}_2\text{O}}^2 \quad (4)$$

in order to obtain the rate constant from the slope of the appropriate plot.

Figure 2 gives examples of the resulting values of k' derived from computerized fitting of decay traces using eqn. (1) for different pressures of N_2O at $T = 667 \text{ K}$ and $T = 783 \text{ K}$. The slope of each plot yields the appropriate value of $k_{\text{N}_2\text{O}}$ for the relevant temperature. The temperature range employed

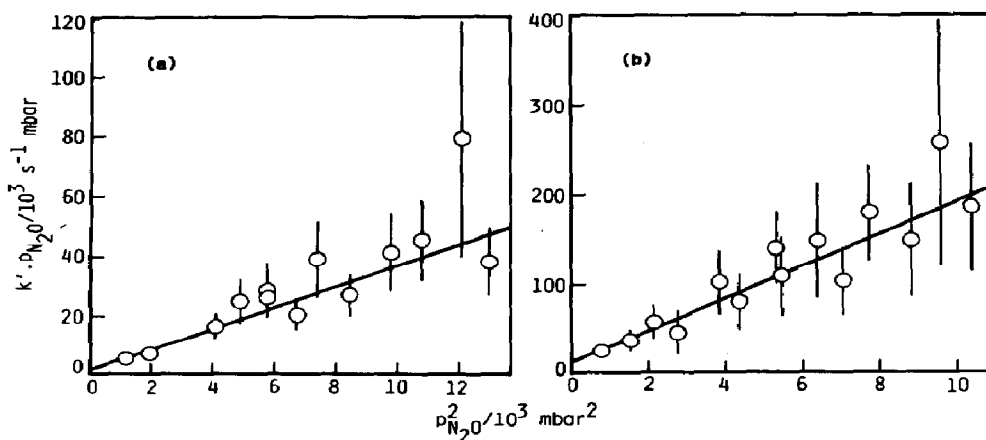


Fig. 2. Variation in $k' p_{\text{N}_2\text{O}}$ vs. $p_{\text{N}_2\text{O}}^2$ of the pseudo-first-order rate coefficient k' for the decay of $\text{Pb}(6^3\text{P}_0)$ in the presence of N_2O following the pulsed irradiation of PbBr_2 vapour at (a) $T = 667 \text{ K}$ and (b) $T = 783 \text{ K}$, indicating the removal of lead atoms by both chemical reaction and diffusion ($E = 16 \text{ J}$).

is restricted at the upper end by the eventual decomposition of the halide precursor and at the lower end by vapour pressures of precursor insufficient to generate significant densities of $\text{Pb}(6^3\text{P}_0)$ for spectroscopic monitoring. The intercepts of the plots of the type given in Fig. 2 in principle yield β at each temperature and hence the value of $D\{\text{Pb}(6^3\text{P}_0)\text{-N}_2\text{O}\}$ via eqn. (3). However, diffusional removal is small compared with chemical loss at the pressures of N_2O typically used for reaction and attempts to determine $D(\text{Pb}\text{-N}_2\text{O})$ are not reported in view of the very large scatter in the resulting values of D'_{12} . Further, we are not concerned here with characterizing small differences in diffusion coefficients for lead atoms in helium and N_2O . In any event, such values are better obtained by recasting eqn. (2) in the form

$$\frac{k'}{p_{\text{N}_2\text{O}}} = \frac{\beta}{p_{\text{N}_2\text{O}}^2} + k_{\text{N}_2\text{O}} \quad (5)$$

and using correspondingly low pressures of N_2O . Nevertheless, we may note that the intercepts of plots of the type given in Fig. 2 are approximately consistent with diffusional removal as found for helium. The results for $k_{\text{N}_2\text{O}}$ at different temperatures are given in Table 1.

Figure 3 shows the data in Table 1 in Arrhenius form ($k_{\text{R}} = A \exp(-E/RT)$), yielding

$$k_{\text{N}_2\text{O}} = 6 \times 10^{-11} \exp\left(\frac{-68 \pm 10 \text{ kJ mol}^{-1}}{RT}\right) \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

The Arrhenius A factor for reaction (I) is reported with an accuracy of a factor of about 2. Such a scatter may be expected for a reaction characterized by a high activation energy, studied at elevated temperatures over a necessarily limited temperature range. This may be compared with various values reported for the analogous reaction



TABLE 1

Absolute second-order rate constants $k_{\text{N}_2\text{O}}$ for the reaction of $\text{Pb}(6^3\text{P}_0)$ with N_2O at various temperatures determined by time-resolved atomic resonance absorption spectroscopy following the pulsed irradiation of PbBr_2 vapour (errors 1σ)

T (K)	$k_{\text{N}_2\text{O}} (\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
648	2.16 ± 0.32
667	3.25 ± 0.37
705	3.87 ± 0.20
719	6.23 ± 0.21
746	9.22 ± 0.49
783	19.5 ± 1.7

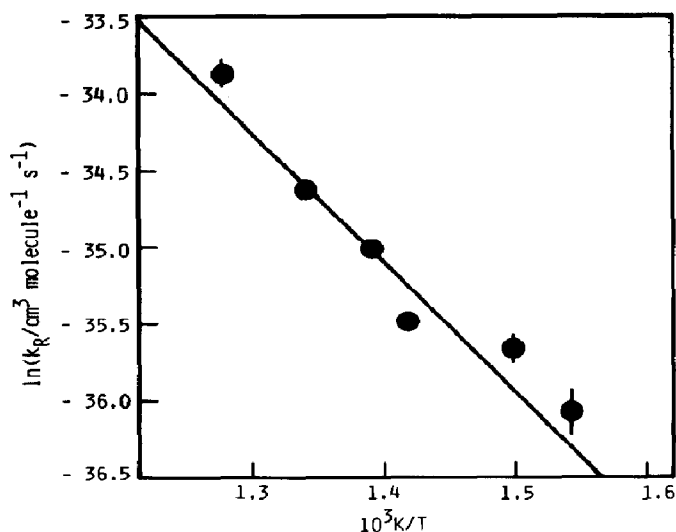


Fig. 3. Arrhenius plot ($\ln k_R$ vs. $1/T$) for the removal of $\text{Pb}(6^3\text{P}_0)$ with N_2O .

($D_0^\circ\{\text{SnO}(X^1\Sigma^+)\} = 5.49 \text{ eV}$ [33]) derived from FPAS measurements of Wiesenfeld and Yuen [10] yielding

$$k_{\text{II}} = (5.0 \pm 1.0) \times 10^{-13} \exp\left(\frac{-33 \pm 2 \text{ kJ mol}^{-1}}{RT}\right) \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

(at 341 - 377 K) and those of Husain and Chowdhury [11] giving

$$k_{\text{II}} = (4.4 \pm 1.6) \times 10^{-13} \exp\left(\frac{-21 \pm 3 \text{ kJ mol}^{-1}}{RT}\right) \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

HTFFR measurements [6] (at 500 - 950 K) yielded

$$k_{\text{II}} = (8.9 \pm 4.0) \times 10^{-13} \exp\left(\frac{-18.9 \pm 1.5 \text{ kJ mol}^{-1}}{RT}\right) \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$$

We may note the greater activation energy for $\text{Pb} + \text{N}_2\text{O}$ compared with that for $\text{Sn} + \text{N}_2\text{O}$, in accord with the difference in thermochemistry. Most striking is the difference in the Arrhenius A factors, that for $\text{Sn} + \text{N}_2\text{O}$ being particularly low and arising from the more restrictive effects of non-adiabatic transitions for the lighter atom, an aspect that can be seen within the context of the diagram correlating the states of $\text{Sn} + \text{N}_2\text{O}$ and $\text{SnO} + \text{N}_2$ given by Wiesenfeld and Yuen [10].

For the lighter element germanium,



($D_0^\circ\{\text{GeO}(X^1\Sigma^+)\} = 6.78 \text{ eV}$ [33]), the Arrhenius parameters are not fully clear. Fontijn and Felder [6, 17] report activation energies (E_{II}) from

HTFFR measurements for the close lying spin-orbit levels in $\text{Ge}(4^3\text{P}_J)$ (which should be in Boltzmann equilibrium throughout reaction) which vary in both magnitude and sign, namely $E_{\text{III}}(J=0) = 4.1 \pm 0.4 \text{ kJ mol}^{-1}$, $E_{\text{III}}(J=1) = -0.8 \pm 0.3 \text{ kJ mol}^{-1}$ and $E_{\text{III}}(J=2) = 1.4 \pm 0.8 \text{ kJ mol}^{-1}$. E_{III} is clearly close to zero. Indeed, Husain and Chowdhury [16] were unable to detect a significant temperature dependence in FPAS measurements over the range 297 - 350 K. For the highly exothermic reactions [2, 33]



only room temperature rate data have been reported from FPAS vacuum UV measurements ($k_{\text{IV}} = (1.9 \pm 0.2) \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ [19] and $k_{\text{V}} = (1.3 \pm 0.3) \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ [21] or $k_{\text{V}} = (2.5 \pm 1.0) \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ [20]).

Finally, we may note that these highly exothermic reactions may yield electronically excited diatomic oxides with subsequent chemiluminescence, a subject considered in some detail by Fontijn and Felder [6]. For example, very large quantum yields have been reported for $\text{SnO}(a^3\Sigma)$ ($\Phi = 0.53 \pm 0.26$) and $\text{SnO}(b^3\Pi)$ ($\Phi = (0.59 \pm 0.29) \exp\{-(1200 \pm 200)/T\}$) following reaction (II), in HTFFR measurements [6]. In the case of reaction (I) ($\Delta H = -17\,450 \text{ cm}^{-1}$ [2, 33]), the $1(16\,025 \text{ cm}^{-1}, a)$ and $0^-(16\,454 \text{ cm}^{-1}, b)$ components of $\text{PbO}(^3\Sigma^+)$ are energetically accessible. Both the dipole-allowed $a \rightarrow X$ and dipole-forbidden $b \rightarrow X$ emissions have been observed from the reaction between lead and O_3 under both single-collision conditions [34] and in a fast flow system [35]. Clearly, chemiluminescence measurements from $\text{Pb} + \text{N}_2\text{O}$, both in the time-resolved mode and in a flow system, especially if coupled with quantum yield determinations including their temperature dependences, would permit the elucidation of pathways to specific electronic states.

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