

TIME-RESOLVED RESONANCE FLUORESCENCE STUDY OF ELECTRONICALLY EXCITED IODINE ATOMS: QUENCHING OF $I(5^2P_{1/2})$ BY HCN, NH_3 AND OCS

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Summary

Quenching of electronically excited iodine atoms $I(5^2P_{1/2})$ by HCN, NH_3 and OCS has been studied at 295 K using time-resolved resonance fluorescence. The quenching efficiency for NH_3 is shown to be relatively high ($k(NH_3) = (2.1 \pm 0.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and it is suggested that quenching occurs via near-resonant electronic to vibration-rotation (E-VR) energy transfer. Quenching by OCS and HCN is less efficient owing to the absence of near-resonant E-VR channels ($k(HCN) = (6.8 \pm 0.7) \times 10^{-14}$; $k(OCS) = (1.6 \pm 0.1) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The use of NH_3 , HCN and OCS in E-VR transfer lasers is discussed briefly.

1. Introduction

Recent reports that electronic to vibration-rotation (E-VR) energy transfer can be utilized to pump semi-tunable IR lasers has aroused considerable interest in this area of energy transfer. Petersen *et al.* [1] have shown that the quenching of electronically excited bromine atoms $Br(4^2P_{1/2})$ by a number of molecules, including CO_2 , HCN, H_2O , N_2O and C_2H_2 , leads to mode-selective excitation and provides a method for down conversion of laser frequencies in the IR region.

E-VR transfer is also known to be efficient [2 - 4] for $I(5^2P_{1/2})$ and it has been shown that quenching by H_2O leads to selective excitation of two stretching quanta with high (near 100%) efficiency [4]. Although quenching efficiencies for $I(5^2P_{1/2})$ are generally lower than for $Br(4^2P_{1/2})$, and thus the possibility of intermolecular energy transfer between the quenching molecules higher, it is still expected that E-VR transfer from $I(5^2P_{1/2})$ will provide a further means of pumping IR molecular lasers [4]. It is therefore of interest to study quenching of $I(5^2P_{1/2})$ by molecules such as NH_3 , HCN and OCS which have large IR transition dipoles; HCN and OCS were thought to

be of interest as they are known to give laser action following E-VR transfer from Br($4^2P_{1/2}$).

In the present work we use time-resolved resonance fluorescence [5] to determine total quenching cross sections. We have shown elsewhere [5] that this is a sensitive and precise technique for studying total cross sections, and that the results can provide considerable insight into quenching mechanisms.

2. Experimental

The experimental arrangement for time-resolved resonance fluorescence has been described in detail previously [5]. It is a relatively simple technique but provides data of higher precision and greater reliability than most other techniques. Flash energies of typically 50 J can be used to produce the excited atoms, which in the present study were derived from the photolysis of C_3F_7I . Resonance fluorescence was produced following excitation ($\lambda = 206.2$ nm) of I($5^2P_{1/2}$) to the $5p^46s(^2P_{3/2})$ level by means of a microwave-powered atomic lamp. A solar-blind photomultiplier was used to monitor the fluorescence as a function of time after the photolysis pulse. We have previously used a conventional photomultiplier, sensitive in the visible and UV regions, to monitor the resonance fluorescence but find that the use of a solar-blind photomultiplier helps to reduce the initial disturbance due to scattered light from the photolysis flash. The output from the photomultiplier was fed to a fast analogue-to-digital converter (Datalab DL905) which was interfaced to a signal averager (Datalab DL4000).

Signal averaging of four to eight shots was used to improve the signal-to-noise ratio which was slightly degraded owing to absorption of the atomic resonance radiation by the quenching molecules, but was not strictly necessary. The contents of the memory of the signal averager could be inspected on a visual display and transferred to punched tape for computer processing.

2.1. Reagents

C_3F_7I (Pierce Chemical Company) and OCS (Matheson) were thoroughly degassed and distilled under vacuum; NH_3 (BOC anhydrous) was dried over sodium and thoroughly degassed; HCN was prepared by standard methods and distilled under vacuum. The purity of all the reagents was checked by IR and mass spectrometric analysis; no significant level of impurity was found.

3. Results

The quenching of I($5^2P_{1/2}$) was studied under pseudo first order kinetic conditions, the partial pressure of quenching gas being several orders of

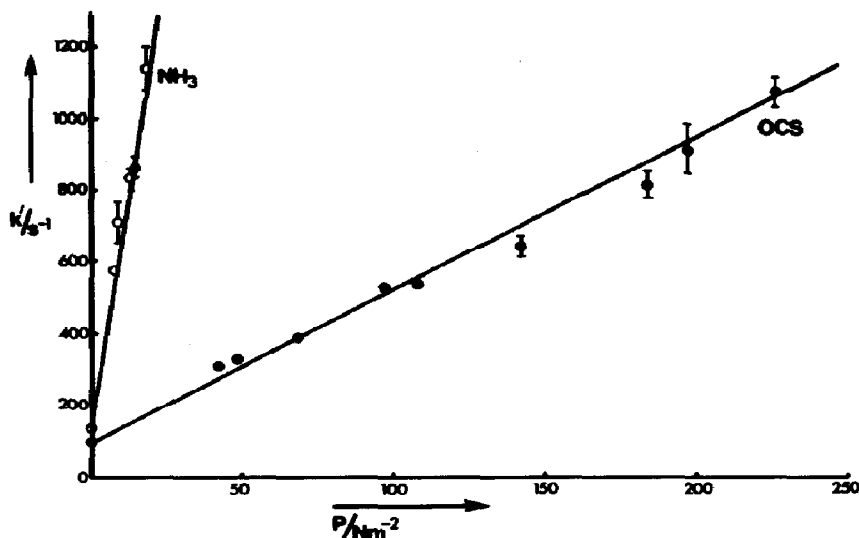


Fig. 1. Quenching of $I(5^2P_{1/2})$ by NH_3 and OCS. Plot of first order rate coefficients k' against pressure: $P(C_3F_7I) = 250 \text{ N m}^{-2}$; $P(\text{total}) = 3.8 \text{ kN m}^{-2}$.

TABLE 1

Second order quenching data for $I(5^2P_{1/2})$ at 295 K

Quenching gas	Second order rate constant ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
NH_3	$(2.1 \pm 0.2) \times 10^{-13}$
HCN	$(6.8 \pm 0.7) \times 10^{-14}$
OCS	$(1.6 \pm 0.1) \times 10^{-14}$
OCS (abs. tech.) ^a	$(2.6 \pm 0.3) \times 10^{-14}$

^a Result obtained using time-resolved absorption spectrophotometry (see text).

magnitude greater than that of the excited atom. Simple exponential decays were observed in all experimental runs in accordance with the expected first order kinetics. First order decay coefficients k' derived from such experiments, which were conducted over a range of quenching gas pressures, are shown in Fig. 1 for OCS and NH_3 . The second order rate constants derived from such plots are given in Table 1.

An earlier result for OCS determined by time-resolved absorption techniques is also given. It can be seen that the result from time-resolved absorption is significantly larger than that determined here using resonance fluorescence. We have previously compared a range of data obtained by the two techniques [6] and have shown that, where the quenching molecule absorbs in the UV and is photolysed, care is needed in deriving data with the absorption technique. It appears that some atomic and free radical

species produced by the flash have high quenching efficiencies and can thus influence the decay kinetics of the excited atom. Such effects are minimized with the resonance fluorescence technique owing to the lower degree of photolysis employed. In the present work we have demonstrated that the effects of photolysis products are entirely negligible by repeating fluorescence decay measurements over a range of flash energies (typically 40 - 100 J)[†]. No significant change in the decay kinetics could be detected for any of the gases studied. It was also found that using the time-resolved fluorescence technique a given mixture could be flashed ten or more times without any significant change in the decay kinetics. This is seldom the case when absorption techniques are used.

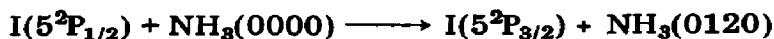
4. Discussion

Of the quenching molecules studied here, NH₃ is potentially the most interesting. The relatively high quenching efficiency for this molecule suggests that it may prove useful in E-VR transfer laser systems pumped by iodine atoms. Development of efficient E-VR transfer lasers requires in general that the rate of transfer to the quenching molecule be more rapid than the rate of intermolecular transfer between quenching molecules. While exceptions to this principle can be envisaged (*e.g.* where a particular vibrational level acts as a "bottleneck" and possesses an appropriate optical transition), it is generally expected that intermolecular or intramolecular relaxation will reduce the efficiency of E-VR laser systems. The low quenching efficiencies for OCS and HCN thus render them less likely candidates for laser use.

We next consider each quenching molecule in turn and try to identify the most likely energy transfer channels involved for the quenching of I(5²P_{1/2}) atoms.

4.1. Quenching by NH₃

There are several near-resonant channels available, involving the excitation of 2ν₃ + ν₂, for quenching of I(5²P_{1/2}) by NH₃, namely



The IR spectrum of NH₃ in the 1.3 μm region has been studied under medium resolution [7] and it is clear that the 2ν₃ + ν₂ band possesses an appreciable transition moment. A high resolution study and analysis of the 1.3 μm band would allow a more detailed discussion of the energy transfer channels involved; however, at the present time we simply note that there are three transitions which lie within 30 cm⁻¹ for resonance with the iodine atom transition (7603.15 cm⁻¹). One line in the NH₃ spectrum lies at almost

[†]Only a small fraction of the light output from the flash is actually absorbed by the reagents in the fluorescence cell as the flash lamp is spaced about 30 cm from the cell.

exact resonance (7602.8 cm^{-1}) with the iodine transition. We would therefore expect fairly efficient E-VR transfer to occur via coupling between the quadrupole transition moment of the iodine atom and the electric dipole transition moment of NH_3 .

4.2. Quenching by HCN

There are no near-resonant channels available for quenching of $\text{I}(5^2\text{P}_{1/2})$ by HCN; the closest transition would involve the excitation of the combination $2\nu_1 + \nu_3$ which is about 200 cm^{-1} off resonance and appears to be very weak as it is not listed by Herzberg [8]. Similar considerations apply to the excitation of the combination $2\nu_3 + \nu_2$ which is about 370 cm^{-1} off resonance. The next higher transitions, involving three quanta, are the combinations $2\nu_3 + \nu_1$ (8586 cm^{-1}) and $3\nu_3$ (9627 cm^{-1}); both of these transitions have been observed in absorption but are endothermic and well off resonance.

Combinations involving four or more quanta can be found [8] which provide resonant E-VR transfer channels but they will have very low transition moments and will therefore be inefficient.

Quenching by HCN can be compared with HCl where again the excitation of three quanta is required and the absence of near-resonant channels leads to a low quenching rate constant [3] ($k(\text{HCl}) = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The quenching mechanism proposed for HCl involves the crossing of potential energy surfaces and it seems likely that quenching by HCN proceeds by the same mechanism.

4.3. Quenching by OCS

Quenching of $\text{I}(5^2\text{P}_{1/2})$ via an E-VR mechanism would require the excitation of four or more vibrational quanta. We would therefore expect the quenching efficiency to be significantly lower than for the other molecules considered here, as is indeed observed. An even lower efficiency is observed [9] for quenching of $\text{I}(5^2\text{P}_{1/2})$ by CO_2 ($k(\text{CO}_2) = 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This contrasts with the situation for $\text{Br}(4^2\text{P}_{1/2})$ with CO_2 where the presence of near-resonant E-VR channels involving excitation of two quanta leads to a high quenching efficiency [10]:



$$k = (1.6 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

These data clearly reveal the rapid decline in efficiency for resonant E-VR transfer with increasing number of quanta excited in the exchange process.

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