

TIME-RESOLVED STUDY OF THE LOWEST OPTICALLY ACCESSIBLE ION-PAIR STATE OF IBr USING SYNCHROTRON RADIATION

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Summary

A time-resolved study of the quenching of the first optically accessible (single photon) ion-pair state of IBr ($E \approx 53\,000\text{ cm}^{-1}$) is reported. Absolute rate constants for quenching of this state by Br_2 and IBr have been determined as $k_{\text{Br}_2} = (6.4 \pm 0.4) \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and $k_{\text{IBr}} = (9.1 \pm 1.4) \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

1. Introduction

The ion-pair states of the halogens ($E \approx 50\,000\text{ cm}^{-1}$) have recently attracted considerable attention [1 - 10]. They exhibit a number of interesting physical, chemical and spectroscopic properties, the most notable of these being that (i) their equilibrium internuclear bond length is greater than that of the ground electronic state although they have significantly stronger bonds, (ii) the most intense emission from the ion-pair states is to unbound regions of the ground state and other low lying states [5, 6], (iii) they are extremely reactive states and are capable of cleaving some of the strongest chemical bonds [1, 3] (e.g. carbon-fluorine bonds) and of reacting with the noble gases [4] and (iv) they undergo interstate transfer with essentially unit collision efficiency, even with helium where momentum matching is extremely poor.

In the present communication, we report absolute rate data for the first optically accessible (single photon) ion-pair state of IBr.

2. Experimental details

Time-resolved studies of the fluorescence from IBr were carried out using the electron storage ring at the SERC Daresbury Laboratory. The

storage ring was operated in single-bunch mode giving light pulses of 200 ps duration with a repetition frequency of 3.1 MHz. The synchrotron radiation was dispersed by a Spex 1500 SP Czerny–Turner monochromator; an excitation wavelength of 188 nm (bandpass, 3 nm) was used for all of the studies presented here. Fluorescence was detected using a Mullard XP2020Q photomultiplier (after passage through an LF30 filter, $\lambda > 300$ nm) at right angles to the excitation beam. Samples were contained in a standard fluorescence cell (1 cm \times 1 cm square cross section) fitted with a greaseless tap. Fluorescence lifetimes were determined by measuring successive time intervals between photomultiplier pulses (after constant fraction discrimination) and the zero-time reference signal from the storage ring, using a time-to-amplitude converter (TAC). Output pulses from the TAC were accumulated in a multichannel analyser. Time spectra were recorded locally on a PDP 11/04 and also transferred to the AS7000 mainframe computer at Daresbury for data storage and analysis.

3. Results and discussion

Two broad oscillatory continuum emission systems are observed in the 270 - 470 nm region when IBr is optically excited at $\lambda \leq 200$ nm [7]. These emissions have been assigned to transitions from an upper ion-pair state to unbound regions of the ground state and to a second state (possibly repulsive) which has yet to be identified. The only clearly defined absorption system around 190 nm is to a Rydberg upper state and it appears that absorption to ion-pair states in this region is much weaker and is thus masked by the stronger Rydberg absorptions. However, it is clear that the observed oscillatory continuum emissions must originate from an ion-pair state and not from a Rydberg state.

Care must be taken to suppress I_2 , which exists in equilibrium with IBr, as it also gives rise to strong fluorescence in the same region. I_2 can be suppressed to an acceptable level by adding excess Br_2 , and in the work reported here sufficient Br_2 was added to reduce the I_2 partial pressure to below 1% of that of IBr.

The decay of IBr fluorescence following excitation at 188 nm with pulsed synchrotron radiation is shown in Fig. 1. These data give an excellent fit to an exponential decay over two decades and the fluorescence lifetime can be obtained with high precision. The residuals shown in the lower half of Fig. 1 illustrate the standard deviation of the experimental points from the curve generated by computer fitting.

We have measured the fluorescence lifetime of IBr for a range of total pressures (see Fig. 2) and by extrapolating this plot to zero pressure we obtain a pure radiative lifetime of 27.1 ± 3.0 ns. The slope of the line in Fig. 2 yields a quenching coefficient which contains terms involving both IBr and Br_2 (i.e. $k' = k_{IBr}[IBr] + k_{Br_2}[Br_2]$). In order to separate these two quenching terms, we have carried out a further series of experiments in

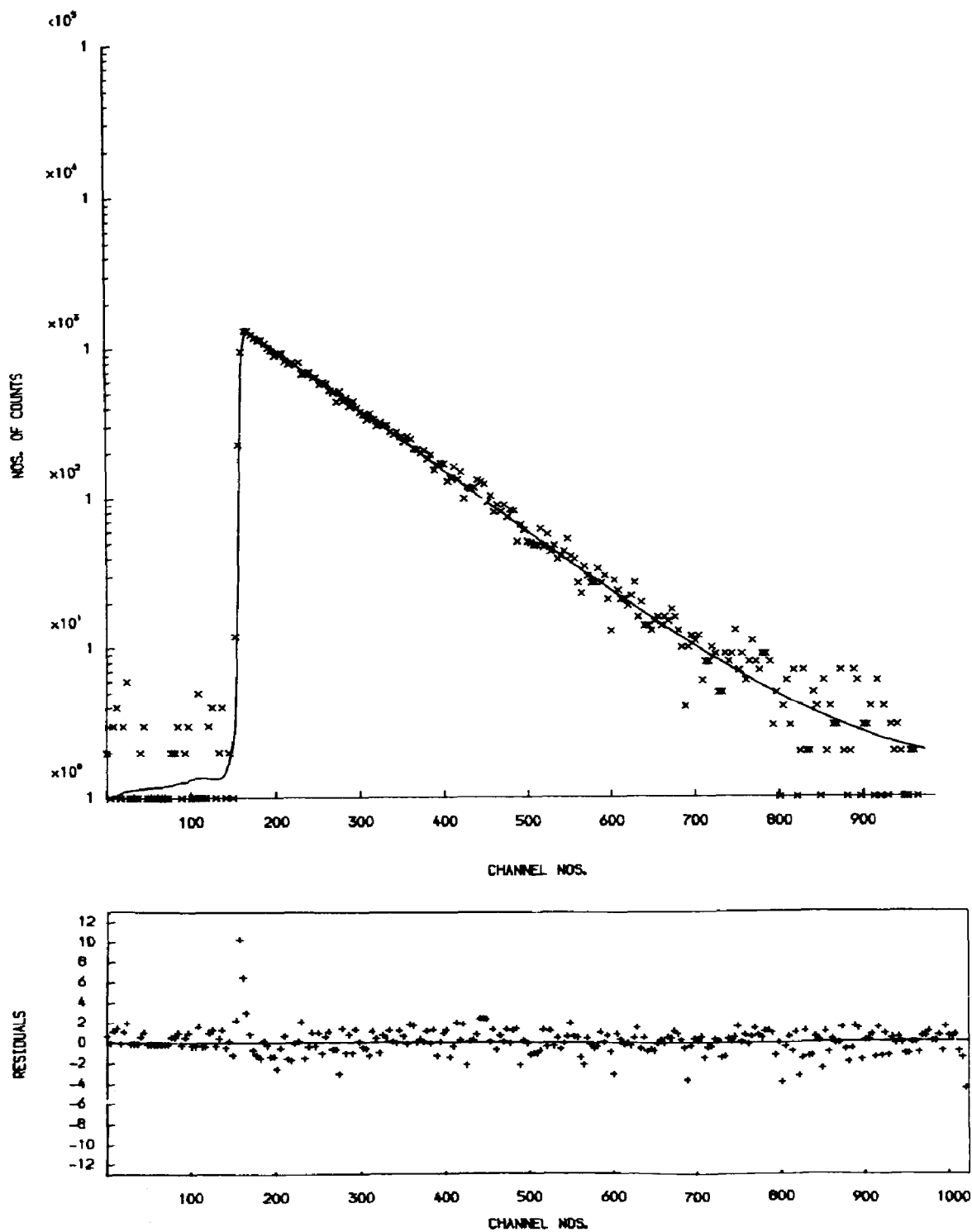


Fig. 1. Decay of fluorescence from IBr (upper trace) following excitation at 188 nm with pulsed synchrotron radiation ($P_{\text{IBr}} = 133 \text{ N m}^{-2}$; $P_{\text{Br}_2} = 266 \text{ N m}^{-2}$; time scale: one channel, 0.1132 ns). The lower trace shows the residuals (see text).

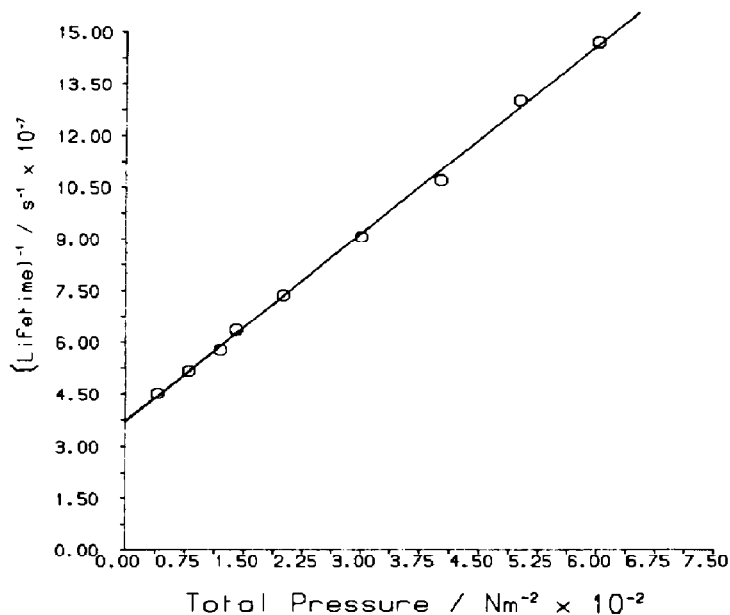


Fig. 2. Plot of the reciprocal of the fluorescence lifetime of IBr against the total pressure of IBr plus Br₂ ($P_{\text{Br}_2} = 2P_{\text{IBr}}$).

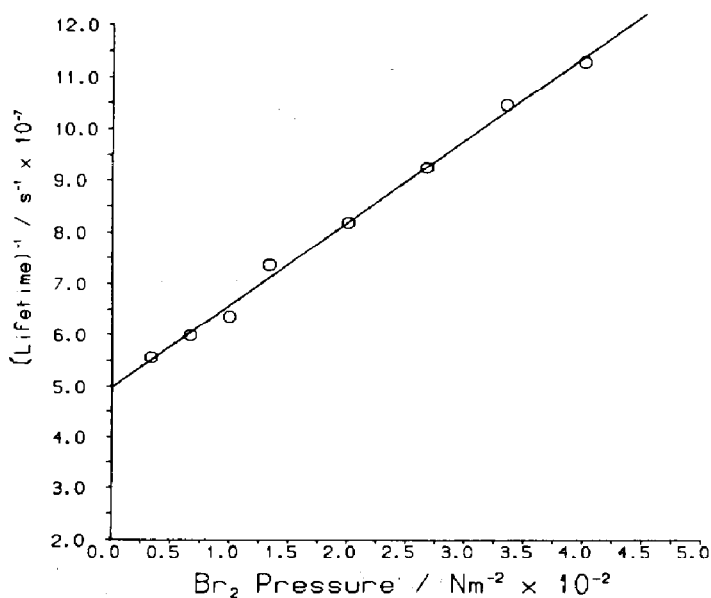


Fig. 3. Plot of the reciprocal of the fluorescence lifetime of IBr in the presence of increasing pressures of Br₂ ($P_{\text{IBr}} = 57 \text{ N m}^{-2}$).

which the partial pressure of IBr was kept constant and the partial pressure of Br₂ varied. These results are shown in Fig. 3. The slope of the plot in Fig. 3 yields a rate constant for quenching of the ion-pair state of IBr by Br₂ of $k_{\text{Br}_2} = (6.4 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Using this value, we were then able to obtain a rate constant for self quenching from the data in Fig. 2. This yields a value of $k_{\text{IBr}} = (9.1 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Both of these values appear at first sight to be larger than the value expected for quenching for unit collision efficiency. However, it should be remembered that ion-pair states have a relatively large equilibrium inter-nuclear separation and also a relatively diffuse outer electron structure. Furthermore, the efficiency of electronic-to-electronic transfer is expected to be high as there will be a number of close-lying ion-pair states which will allow near-resonant transfer to occur.

Further work on quenching by other species is in progress.

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