

ION-PAIR ($\text{Br}^+ + \text{Br}^-$) FORMATION FROM PHOTODISSOCIATION OF Br_2 NEAR THE FIRST IONISATION LIMIT

Andrew J. YENCHA¹, Devinder K. KELA

Department of Chemistry, State University of New York at Albany, Albany, NY 12222, USA

Robert J. DONOVAN

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

Andrew HOPKIRK

SERC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

and

Agust KVARAN

Science Institute, University of Iceland, 107 Reykjavik, Iceland

Received 14 October 1989; in final form 1 November 1989

Excitation functions for Br^- and Br^+ formation from jet-cooled Br_2 , in the region 120–114 nm (i.e. from threshold to above the ionisation limit of Br_2), are reported. The mechanism for ion-pair formation is discussed in terms of homogeneous coupling between the $8p\pi$ Rydberg state and the $\text{D}(0_v^+)$ ion-pair state, correlating with $\text{Br}^- (^1\text{S}_0) + \text{Br}^+ (^3\text{P}_2)$.

1. Introduction

It is clear from thermodynamic data and also from experimental studies [1–3] that ion-pair formation ($\text{X}^+ + \text{Y}^-$) can occur below the ionisation threshold of the halogen and interhalogen molecules (the only exception being Cl_2 [4]). Early spectroscopic studies at low resolution, by Morrison and co-workers [1], demonstrated the formation of Br^+ ions just below the ionisation limit for the Br_2 molecule. A higher resolution excitation spectrum for Br^+ formation was presented in reports by Dibeler et al. [5,6], but no discussion was given.

In the present work we report the excitation spectra for both Br^- and Br^+ formation from jet-cooled Br_2 , in the region below and just above the first ionisation limit (i.e. 114–120 nm), obtained using tunable synchrotron radiation. These excitation spectra

are found to be remarkably simple in structure, especially when one considers the high density of electronic states present in the vicinity of the first ionisation limit.

2. Experimental

The results presented here were obtained using tunable synchrotron radiation on beam line 11 of the National Synchrotron Light Source (NSLS) facility of the Brookhaven National Laboratory. The molecular beam apparatus and its general operating conditions for producing photoabsorption ion yield spectra have been described in detail previously [7,8], thus only a brief report will be given here.

Synchrotron light emanating from the 750 MeV electron storage ring at NSLS was dispersed using a 4 m monochromator (1200 lines/mm grating) before passing through a 2 mm thick LiF filter, used to

¹ Also Department of Physics.

eliminate second- and higher-order radiation, and the entrance slit of the apparatus. All results presented here employed light with a wavelength band pass of 0.09 nm. Radiation intersecting the molecular beam was monitored using a sodium salicylate quantum converter plus photomultiplier. This arrangement enabled us to normalize the measured mass/charge ion intensities from the quadrupole mass spectrometer, thereby correcting for the decay with time of the synchrotron light and the wavelength dependence of the monochromator. For negative ion measurements, it was found necessary to place two permanent magnets (with an effective field of ≈ 10 G) on opposite sides of and midway along the quadrupole mass spectrometer (outside the vacuum system) to suppress electrons from being collected by the channeltron multiplier at wavelengths below the ionisation limit. Typically, an electron background of < 20 cps could be achieved in this manner.

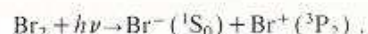
The molecular beam was formed by passing a $\approx 4\%$ mixture of Br_2 (J.T. Baker Co.) in He through a heated (100°C) glass nozzle of $200\ \mu\text{m}$ diameter and an ambient temperature, 1 mm diameter, skimmer located ≈ 5 – 10 mm downstream of the nozzle. The nozzle pressure of this mixture was adjusted to obtain the maximum ion intensity. Typically, this was achieved at ≈ 70 Torr as measured on a capacitance manometer. At nozzle pressures greater than this the ion signal decreased, presumably due to cluster formation.

The wavelength scale of the synchrotron-light monochromator was calibrated by setting the zero at the maximum of the zero-order radiation. The accuracy of this calibration was further checked and the resolution determined by recording the photoionization yield spectrum of argon. In this manner, we found the wavelength scale to be accurate to within ± 0.02 nm. Photoabsorption ion yield curves were obtained using standard pulse counting procedures, a CAMAC interface and a PDP 11/23 minicomputer.

3. Results and discussion

The excitation functions for Br^- and Br^+ formation from Br_2 , together with the parent molecule photoionisation function, are shown in fig. 1. Clearly,

both Br^- and Br^+ are formed via the same process as the excitation functions are the same, within experimental limits. The threshold for ion-pair formation can be estimated from available thermodynamic data as $84059\ \text{cm}^{-1}$ (equivalent to 118.96 nm). The observed threshold (118.73 nm) is only slightly greater than the thermodynamic threshold for the process,



The small peak at 119.2 nm, is assigned to hot band absorption.

In table 1 are given the peak positions and energy separations for Br^+ and Br^- formation. The average separation between the peaks in these excitation functions is $344 \pm 16\ \text{cm}^{-1}$, which is typical for a Rydberg state of Br_2 . A high density of Rydberg states exists in this region (rising to infinity at the Br_2 ionisation limit) and the most surprising feature of the observed excitation functions is the simplicity of their structure. A quasi-continuous excitation function might well have been expected, a priori.

Because of the striking similarity between the Br^+ and Br^- excitation functions shown in fig. 1 and the photoelectron spectrum for formation of the two spin-orbit components of the Br_2^+ ground state ion [9,10], we have carried out a series of Franck-Condon factor calculations for transitions to a Rydberg state to compare with the observed excitation functions. Wavefunctions were calculated by numerical integration of the radial Schrödinger equation for the known ground state potential and a simple Morse potential (in cm^{-1}) for the Rydberg state:

$$U(r) = T_e + D' \{1 - \exp[\beta(r - r_e)]\}^2 .$$

where $T_e = 84226\ \text{cm}^{-1}$, $D' = 23529.8\ \text{cm}^{-1}$, $\beta = 17.2105429\ \text{nm}^{-1}$ and $0.219 < r_e < 0.22\ \text{nm}$. These simulations readily reproduce the peak positions in the observed excitation functions and gave similar overall intensity distributions (see fig. 2). However, closer examination of the intensity distributions shows that, while a good fit between the observed and simulated spectra can be obtained separately at either the short or long wavelength limits, a good overall fit cannot be obtained (see fig. 3).

It would not be surprising if the intensity of the observed excitation functions fell below that of the

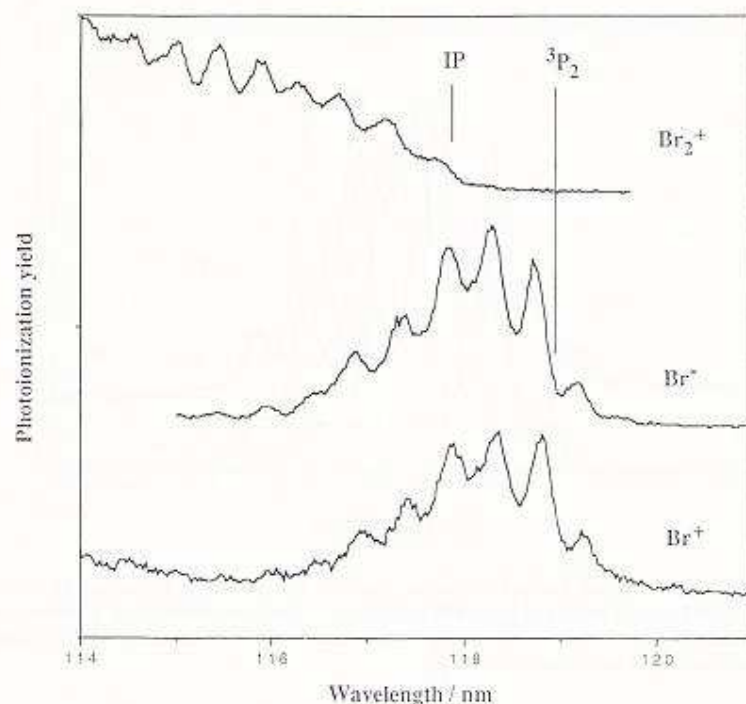


Fig. 1. Excitation functions for Br^- and Br^+ formation together with the ionisation function for the parent molecule, Br_2 . The threshold for formation of $\text{Br}^- (^1\text{S}_0) + \text{Br}^+ (^3\text{P}_2)$ is indicated together with the adiabatic ionisation potential of Br_2 .

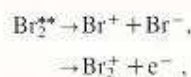
Table 1
Peak positions in the excitation functions for Br^+ and Br^- ion-pair formation

v', v''^{-1}	Wavelength (nm)	Energy (cm^{-1})	Separation ^{b)} (cm^{-1})
0, 2	119.59	83619	302
0, 1	119.16	83921	304
0, 0	118.73	84225	284
1, 0	118.33	84509	323
2, 0	117.88	84832	383
3, 0	117.35	85215	350
4, 0	116.87	85565	316
5, 0	116.44	85881	363
6, 0	115.95	86244	389
7, 0	115.43	86633	

^{a)} Assignment based on simulation calculations (see text).

^{b)} Average separation for the $(v', 0)$ series = $344 \pm 16 \text{ cm}^{-1}$, where the error limits represent the standard deviation from the mean by the variance method.

simulated functions at higher energies, as competition between the two processes.



becomes possible below 117.9 nm. However, when the intensities of the two lowest energy peaks ($> 117.9 \text{ nm}$), in the $v'' = 0$ series, are made to fit in the simulations (fig. 3b), the intensities of bands at higher energy become *less* than the observed intensities. Competition caused by the opening of the ionisation channel would lead to the opposite effect. This strongly suggests that coupling between the Rydberg state and the ion-pair state, that ultimately dissociates to $\text{Br}^+ + \text{Br}^-$, modifies the absorption profile. This is not surprising if the homogeneous coupling between the two states is strong, and all the available evidence points towards this conclusion (see below). One can account for the observed excitation

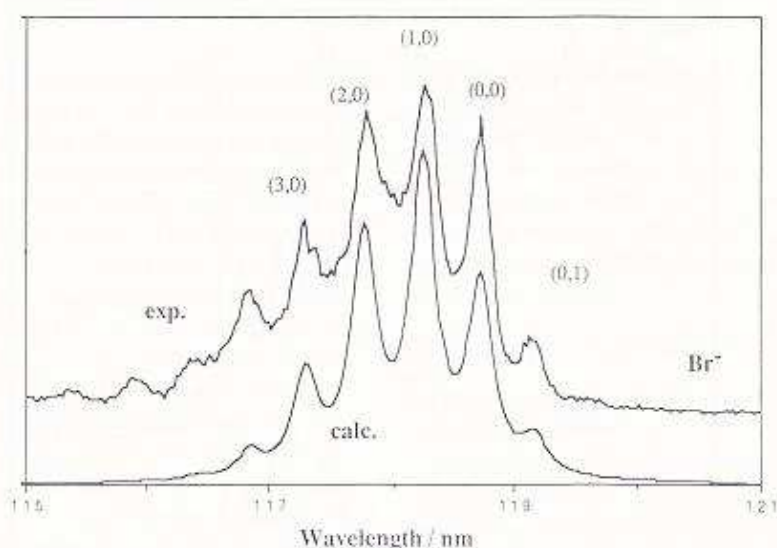


Fig. 2. Observed (upper) and simulated (lower) excitation functions for $\text{Br}^- (\text{Br}^+)$ formation. In the simulation calculation $r_c(\text{Br}_2^{*+}) = 2.198 \text{ \AA}$ and $\omega_c(\text{Br}_2^{*+}) = 343 \text{ cm}^{-1}$ and $\omega_{c,v_c}(\text{Br}_2^{*+}) = 1.25 \text{ cm}^{-1}$. Each calculated (v', v'') band is plotted as a Lorentzian-shaped peak with band width of 88 cm^{-1} . The population ratio in ground state vibrational levels $v'' = 1$ and $v'' = 0$ ($N(v'' = 1)/N(v'' = 0)$) is 0.15, corresponding to a vibrational temperature of 250 K.

function intensity profile by recognising that it is derived from the product of the Franck–Condon factors for excitation to the Rydberg state and a vibrational wavefunction overlap term involving the coupled Rydberg and ion-pair states. Alternatively, it may be more correct to think of the primary absorption process as involving a transition to a *mixed* Rydberg/ion-pair state, of *resonance*, lying in the ion-pair continuum, which would automatically lead to a modified absorption profile.

We next attempt to identify the Rydberg state or states responsible for the observed excitation functions. It is well known that the oscillator strength for transitions to Rydberg states declines very steeply with increasing principal quantum number (i.e. $I \approx n^{-3}$) [11] due to the increasingly diffuse nature of the electronic wavefunction and the consequent poor overlap with the ground state function. We therefore expect Rydberg states with the lowest possible value for the principal quantum number (n) to be strongly favoured. The Rydberg states of Br_2 have been investigated in some detail by Venkateswarlu [12] and long series converging to the first and second ionisation limits have been reported. The state responsible for the structure in the Br^-/Br^+ exci-

tation functions would require $n \approx 16$ if it belonged to a series converging to the first ($^2\Pi_{3/2g}$) ionisation limit, or $n \approx 8$ if it belonged to a series converging to the second ($^2\Pi_{1/2g}$) limit. From the foregoing it is clear that the latter is favoured. Venkateswarlu's high resolution spectrum in this region appears very congested, [12] as expected close to the Rydberg series limit. However, a regularly spaced set of strong diffuse bands is apparent from his published spectrum. Both absorption and fluorescence excitation spectra at medium resolution, where these diffuse (broad) bands stand out more clearly, have been obtained [13]. The peaks in the absorption and fluorescence excitation spectra coincide, but the peaks in the Br^+/Br^- excitation functions are displaced to the blue by about 85 cm^{-1} , reducing the overlap with the absorption peaks. This suggests that the broad bands seen in absorption involve more than one overlapping Rydberg series.

Venkateswarlu has identified seven Rydberg series of ungerade symmetry leading to the ($^2\Pi_{1/2g}$) ionization limit (designated i, j, ℓ , n, r, u and v) [12]. The first four of these involve np Rydberg electrons, while the latter three involve nf Rydberg electrons. Using a value of 87645 cm^{-1} for the ($^2\Pi_{1/2g}$) con-

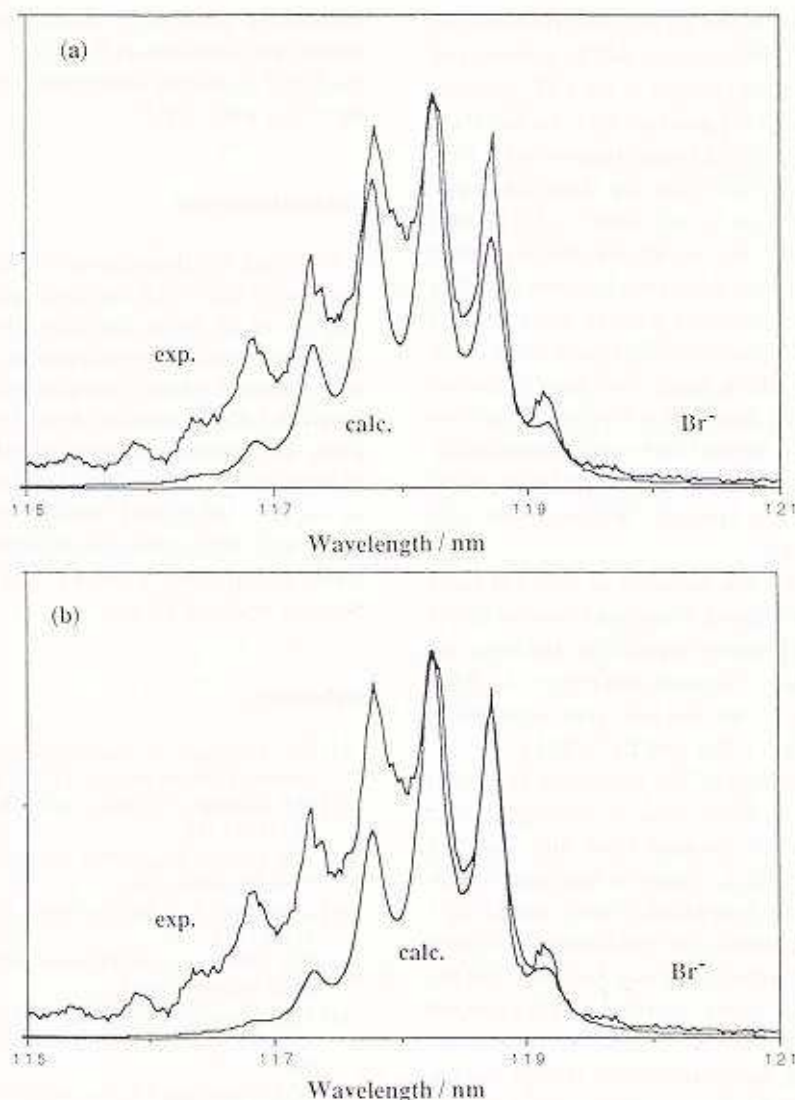


Fig. 3. Observed (upper) and simulated (lower) excitation functions for $\text{Br}^-(\text{Br}^+)$ formation normalized to the most intense band at different values of $r_c(\text{Br}_2^{**})$. In (a) $r_c(\text{Br}_2^{**}) = 2.198 \text{ \AA}$ and in (b) $r_c(\text{Br}_2^{**}) = 2.213 \text{ \AA}$. All other conditions are the same as in fig. 2.

vergence limit, derived from our measured^{#1} IP of Br_2 as 84825 cm^{-1} plus the reported spin-orbit splitting in the Br_2^+ ground state of 2820 cm^{-1} [10], and quantum defects taken from atomic bromine ($\delta \approx 2.5\text{--}2.6$ for $n\text{p}$ Rydberg electrons and $\delta \approx 0$ for $n\text{f}$ Rydberg electrons), we have calculated the $(0, 0)$ band positions of all members of these seven series

^{#1} This value agrees with the revised value given in ref. [5].

up to $n=10$. Our calculations which agree reasonably well with the measured positions for the $n=5$ band in the $n\text{f}$ series and the $n=5\text{--}7$ bands in the $n\text{p}$ series of Venkateswarlu [12], show that the 8p group would lie very close in energy to the first prominent band in the Br^+/Br^- excitation functions shown in fig. 1. On the other hand, the $n\text{f}$ series would not seem to correlate at all well with our observed excitation functions. Excluding the $n\text{f}$ Rydberg series on this

basis, we next consider the $n\pi$ series in more detail. Both $n\pi\sigma$ and $n\pi\pi$ configurations will be present and when these electrons are coupled to the ($^2\Pi_{1/2g}$) core, under Ω - ω coupling, they produce $0u^+$, $1u$ and $0u^+$, $1u(1)$, $1u(2)$, $2u$ Rydberg states, respectively. Venkateswarlu [12] has identified the observed (optically allowed) series as $i(1u)$, $j(0u^+)$, $l(1u)$ and $n(0u^+, 1u)$. Of these four series, we tend to favour the involvement of the $n\pi\pi$ series, because coupling of the Rydberg state or states with an ion-pair state (with the 1441 configuration^{#2}) would involve, in the case of a π -Rydberg state, two parallel transitions, whereas in the case of a σ -Rydberg state, one transition would be parallel and one perpendicular. This leads to the conclusion that the states involved are most probably the $8\pi\pi(0_u^+)$ Rydberg state and $D(0_u^+)$ ion-pair state.

Finally we address the question of how the pairs of ions are actually formed. It is clear from the above discussion that the primary absorption step is not directly to the ion-pair continuum but rather to a Rydberg state that lies in the ion-pair state continuum (correlating with $Br^- (^1S_0)$ and $Br^+ (^3P_2)$).

The smooth envelope of the excitation functions suggests that the Rydberg state is homogeneously predissociated by the ion-pair state and that the crossing or near-crossing occurs on the inner repulsive limbs of the two potentials. Clearly the $D(0_u^+)$ ion pair state that causes the predissociation must cross lower Rydberg states (e.g. $n=5, 6$ and 7) of the same symmetry and strong interactions are expected here also. Evidence for this is seen from the fluorescence excitation spectrum which results via energy transfer from Rydberg excited atoms to Br_2 . These excited Rydberg atoms must be formed via the avoided crossings on the long range portion of the attractive branches of the respective potentials.

In summary, the observed structure in the excitation functions of Br^- and Br^+ in the region of the first ionisation limit, is ascribed to Rydberg/ion-pair

resonances, formed by homogeneous coupling between the (zero-order) $8\pi\pi(0_u^+)$ Rydberg state and the $D(0_u^+)$ ion-pair state which dissociates to yield $Br^- (^1S_0) + Br^+ (^3P_2)$.

Acknowledgement

We thank the Brookhaven National Laboratory for the use of the NSLS facilities and Dr. J.R. Grover and Dr. M.G. White for their advice and assistance in carrying out these experiments. We also thank Dr. K.P. Lawley for many stimulating discussions and in particular for advice on Rydberg to ion-pair coupling. We gratefully acknowledge the partial support of these studies by a State University of New York at Albany (SUNYA) faculty research fellowship grant, a SUNYA Office for Research Grant; a NATO travel Grant (No. 870878), and a NSLS Faculty/Student research Grant.

References

- [1] J.D. Morrison, H. Hurzeler, M.G. Inghram and H.E. Stanton, *J. Chem. Phys.* 33 (1960) 821.
- [2] M.E. Akopyan, F.I. Vilesov and Yu.L. Sergeev, *Opt. Spectry.* 35 (1973) 472.
- [3] V.H. Dibeler, J.A. Walker and K.E. McCulloh, *J. Chem. Phys.* 50 (1969) 4592.
- [4] J. Berkowitz, C.A. Mayhew and B. Rušćić, *Chem. Phys.* 123 (1988) 317.
- [5] V.H. Dibeler, J.A. Walker and K.E. McCulloh, *J. Chem. Phys.* 53 (1970) 4715.
- [6] V.H. Dibeler, J.A. Walker, K.E. McCulloh and H.M. Rosenstock, *Intern. J. Mass Spectrom. Ion Phys.* 7 (1971) 209.
- [7] M.G. White and J.R. Grover, *J. Chem. Phys.* 79 (1983) 4124.
- [8] J.R. Grover, E.A. Walters, J.K. Newman and M.G. White, *J. Am. Chem. Soc.* 107 (1985) 7329.
- [9] A.W. Potts and W.C. Price, *Trans. Faraday Soc.* 67 (1971) 1242.
- [10] A.B. Cornford, D.C. Frost, C.A. McDowell, J.L. Ragle and I.A. Stenhouse, *J. Chem. Phys.* 54 (1971) 2651.
- [11] J. Berkowitz, *Photoabsorption, photoionization and photoelectron spectroscopy* (Academic Press, New York, 1979) pp. 18-21.
- [12] P. Venkateswarlu, *Can. J. Phys.* 47 (1969) 2525.
- [13] D.I. Austin, Ph.D. Thesis, University of Edinburgh (1987).

^{#2} The orbital occupancy is designated (1441) to signify ($\sigma_g^2 \pi_u^4 \pi_g^4 \sigma_u^1$).