Matrix Raman Spectrum and Structure of the Tribromine Radical, Br$_3$

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Matrix isolation infrared spectroscopy has been widely used to provide spectra for highly reactive species frozen at low temperatures in inert gas matrices. Using this technique, evidence was recently cited for the existence and molecular structures of xenon dichloride$^1$ and trichlorine,$^2$ produced in the microwave discharges of xenon–chlorine and krypton–chlorine mixtures, respectively.

Matrix Raman spectroscopy has recently been shown to be a viable technique.$^3$$^4$ In this letter we are reporting for the first time the matrix Raman spectra of the products of Ar/Br$_3$, Kr/Br$_3$, and Xe/Br$_3$ microwave discharge reactions.

The experiments were performed with inert gas to halogen ratios of 60–25:1. Each experiment was performed at least twice to insure reproducibility. In the experiments done with both Kr and Xe, a single Raman line was observed at 197 cm$^{-1}$ (for krypton matrices) and 190 cm$^{-1}$ (for xenon matrices) (apart from the Br$_2$ line at 303 cm$^{-1}$) corresponding to the $\Sigma_g^+$ mode. This band was not observed in unmicro-waved Kr/Br$_3$ and Xe/Br$_3$ mixtures (Figs. 1 and 2). The sensitivity conditions were such that we had at least a factor of 10 to spare, but no other Raman lines could be observed in the range 300–50 cm$^{-1}$.

In diffusion controlled warm up experiments in the temperature range 4.2–50$^\circ$K, the Raman lines at 197 and 191 cm$^{-1}$ showed a marked decrease in intensity while the Br$_2$ line increased in intensity, indicating that the species produced from the discharge was decomposing into bromine upon heating and diffusion. The matrix Raman spectrum of the products of three experiments involving the discharge of Ar/Br$_3$ mixtures (in the ratio of 50:1) showed only extremely weak nonreproducible features in the region of 200 cm$^{-1}$.

We discount the possibility of the species being inert gas bromides since the species were produced in krypton discharges, whereas only the fluorides of krypton are known, and similar experiments performed with Kr/Cl$_2$ mixtures have failed to produce KrCl$_2$.

![Fig. 1. The matrix Raman spectrum of the products of a Kr/Br$_3$ (50:1) microwave discharge C frozen at 4.2$^\circ$K; B and A allowed to diffuse at 35$^\circ$K for 3 and 6 min., respectively, and then recooled to 4.2$^\circ$K.](image-url)
which should be more stable than KrBr$_2$ or KrBr$$. We also discount the possibility of the compound being Br$_4$$$, since this molecule should exhibit two observable Br$-$Br stretches (both $a_1$ if a $T$ shape, proposed for other tetrahalogenes$^4$ is assumed) in the region 150–300 cm$^{-1}$ [note that six Raman active modes are predicted for $T$ shaped (C$_s$) Br$_4$ in the range 200–60 cm$^{-1}$]. Thus, we assign the band at approximately 190 cm$^{-1}$ to the totally symmetrical stretching mode ($\Sigma_2^+$) of the linear ($D_{\infty h}$) symmetrical Br$_3^-$ radical (note that $\nu_1$ of Br$_3^-$ has been observed$^5$ in solution Raman experiments at 162 cm$^{-1}$).

As far as the authors can be certain, vibrational spectroscopic or structural data have not been previously available for Br$_3$, although its existence has been postulated from gas phase bromine atom recombination studies and from molecular beam kinetic data.$^6$ From the temperature dependence of the halogen atom recombination rates, the dissociation energy has been estimated as 3 kcal/mole for Br$_3$ and 1 kcal/mole for Cl$_3$.

The predicted instability of Cl$_3$ relative to Br$_3$ in the above results is reflected in our experiments. In four discharge experiments using Kr/Cl$_3$ ratios of 100–20:1 we could not obtain any evidence for Cl$_3$. Although in our experiments we obtained no evidence for Cl$_3$, it is possible that the local heating effect of the laser beam is enough to destroy it, a complication that would not occur in the infrared. We feel, however, that this is unlikely as we used as little as 10 mW of 5682-Å laser power, under which conditions we have previously obtained Raman spectra for Br$_3$ and XeCl$_3$.

The Raman frequency for matrix isolated Br$_3$ yields a value of 1.70 mdyn/Å for the force constant sum $f_r+f_m$. This value when compared with $f_r=2.45$ mdyn/Å for Br$_2$ and $f_r+f_m=1.23$ Å for Br$_3^-$ provides evidence that the bonding$^7$ in linear Br$_3$ is intermediate between Br$_3^-$ and Br$_2$.

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