

Matrix Raman Spectrum and Structure of the Tribromine Radical,  $\text{Br}_3$ 

D. H. BOAL AND G. A. OZIN\*

*Lash Miller Chemistry Laboratory and Erindale College, University of Toronto, Toronto, Ontario, Canada*

(Received 31 March 1971)

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<sup>1</sup> and trichlorine,<sup>2</sup> 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.<sup>3-5</sup> In this letter we are reporting for the first time the matrix Raman spectra of the products of Ar/ $\text{Br}_2$ , Kr/ $\text{Br}_2$ , and Xe/ $\text{Br}_2$  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  $197\text{ cm}^{-1}$  (for krypton matrices) and  $190\text{ cm}^{-1}$  (for xenon matrices) (apart from the  $\text{Br}_2$  line at  $305\text{ cm}^{-1}$ ) corresponding to the

$\Sigma_g^+$  mode. This band was not observed in unmicro-waved Kr/ $\text{Br}_2$  and Xe/ $\text{Br}_2$  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  $300\text{--}50\text{ cm}^{-1}$ .

In diffusion controlled warm up experiments in the temperature range  $4.2\text{--}50^\circ\text{K}$ , the Raman lines at  $197$  and  $191\text{ cm}^{-1}$  showed a marked decrease in intensity while the  $\text{Br}_2$  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/ $\text{Br}_2$  mixtures (in the ratio of 50:1) showed only extremely weak nonreproducible features in the region of  $200\text{ cm}^{-1}$ .

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/ $\text{Cl}_2$  mixtures have failed to produce KrCl<sub>2</sub>,

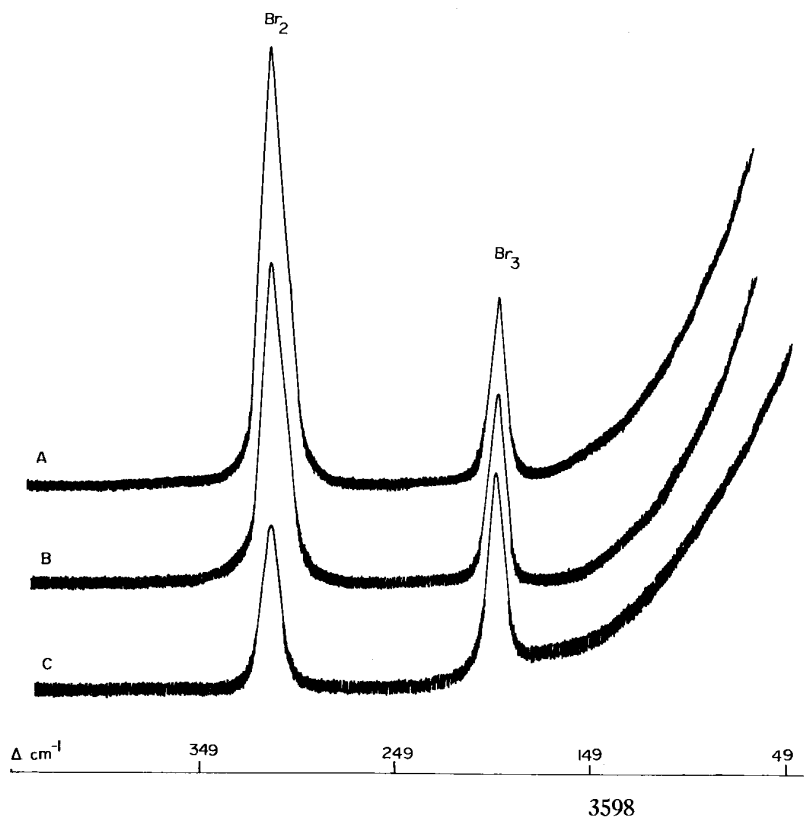


FIG. 1. The matrix Raman spectrum of the products of a Kr/ $\text{Br}_2$  (50:1) microwave discharge C frozen at  $4.2^\circ\text{K}$ ; B and A allowed to diffuse at  $35^\circ\text{K}$  for 3 and 6 min., respectively, and then re-cooled to  $4.2^\circ\text{K}$ .

which should be more stable than  $\text{KrBr}_2$  or  $\text{KrBr}$ . We also discount the possibility of the compound being  $\text{Br}_4$ , since this molecule should exhibit two observable Br-Br stretches (both  $a_1$  if a  $T$  shape, proposed for other tetrahalogens,<sup>6</sup> is assumed) in the region 150–300  $\text{cm}^{-1}$  [note that six Raman active modes are predicted for  $T$  shaped ( $C_{2v}$ )  $\text{Br}_4$  in the range 200–60  $\text{cm}^{-1}$ ]. Thus, we assign the band at approximately 190  $\text{cm}^{-1}$  to the totally symmetrical stretching mode ( $\Sigma_g^+$ ) of the linear ( $D_{\infty h}$ ) symmetrical  $\text{Br}_3$  radical (note that  $\nu_1$  of  $\text{Br}_3^-$  has been observed<sup>7</sup> in solution Raman experiments at 162  $\text{cm}^{-1}$ ).

As far as the authors can be certain, vibrational spectroscopic or structural data have not been previously available for  $\text{Br}_3$ , although its existence has been

postulated from gas phase bromine atom recombination studies and from molecular beam kinetic data.<sup>8</sup> From the temperature dependence of the halogen atom recombination rates, the dissociation energy has been estimated as 3 kcal/mole for  $\text{Br}_3$  and 1 kcal/mole for  $\text{Cl}_3$ .

The predicted instability of  $\text{Cl}_3$  relative to  $\text{Br}_3$  in the above results is reflected in our experiments. In four discharge experiments using  $\text{Kr}/\text{Cl}_2$  ratios of 100–20:1 we could not obtain any evidence for  $\text{Cl}_3$ . Although in our experiments we obtained no evidence for  $\text{Cl}_3$ , 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  $\text{Br}_3$  and  $\text{XeCl}_2$ .

The Raman frequency for matrix isolated  $\text{Br}_3$  yields a value of 1.70  $\text{mdyn}/\text{Å}$  for the force constant sum  $f_r+f_{rr}$ . This value when compared with  $f_r=2.45$   $\text{mdyn}/\text{Å}$  for  $\text{Br}_2$  and  $f_r+f_{rr}=1.23$   $\text{Å}$  for  $\text{Br}_3^-$  provides evidence that the bonding<sup>9</sup> in linear  $\text{Br}_3$  is intermediate between  $\text{Br}_3^-$  and  $\text{Br}_2$ .

We wish to thank the National Research Council of Canada for a NRC Scholarship (D.B.) and financial support.



FIG. 2. The matrix Raman spectrum of the products of a  $\text{Xe}/\text{Br}_2$  (50:1) microwave discharge A frozen at 4.2°K; B allowed to diffuse at 35°K for 3 min. and then recooled to 4.2°K.

<sup>1</sup> L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.* **6**, 1758 (1967).

<sup>2</sup> L. Y. Nelson and G. C. Pimentel, *J. Chem. Phys.* **47**, 3671 (1967).

<sup>3</sup> D. Boal and G. A. Ozin, *Spectry. Letters* **4**, 43 (1971).

<sup>4</sup> D. Boal, G. Briggs, H. Huber, G. A. Ozin, E. A. Robinson, and A. Vander Voet, *Nature* **231**, 174, 1971.

<sup>5</sup> H. Huber and G. A. Ozin, "The Matrix Raman Spectrum Structure, and Bonding in Lithium Superoxide,  $\text{LiO}_2$ " (to be published).

<sup>6</sup> L. Y. Nelson and G. C. Pimentel, *Inorg. Chem.* **7**, 1695 (1968).

<sup>7</sup> W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneis, *J. Chem. Phys.* **35**, 908 (1961).

<sup>8</sup> Y. T. Lee, P. R. LeBreton, J. D. McDonald, and D. R. Herschback, *J. Chem. Phys.* **51**, 455 (1961), and references therein.

<sup>9</sup> G. C. Pimentel, *J. Chem. Phys.* **19**, 446 (1951).