

Figure 1. Tracing of oscilloscope photograph of light transmitted through and emitted from liquid KCl-KBr at 10,600 Å.: A, absorption signal; B, fluorescence signal, same gain as A; C, electron-beam current monitor signal.

signal could then be corrected by subtracting algebraically from it the corresponding fluorescence signal. The absorption was found to show a rise toward the infrared with a possible maximum near 10,000–11,000 Å., and the behavior was similar for both samples. The decay of the optical density shows a long-lived component with a time constant of  $\sim 7 \mu\text{sec}$ . Measurements on an empty tube showed that the silica container was not involved in these effects. No permanent absorption was observed: using chopped light and an a.c. amplifier and recorder, no absorption greater than 1% could be seen 1 sec. after delivering a dose of  $10^6$  rads. When allowed to cool in the absence of irradiation, the resulting crystals were not colored.

The absorption is thought to be similar to that produced by dissolving alkali metals in fused alkali halides. Mollwo<sup>3</sup> found an absorption with a broad maximum at  $\sim 10,000$  Å. for liquid KCl and KBr treated with alkali metal vapor. The absorption is tentatively attributed to a solvated electron or *F* center. The establishment of this identification will require further experiments both on metal solutions and by pulse radiolysis techniques.

(3) E. Mollwo, *Nachr. Akad. Wiss. Göttingen, Math-Physik Kl. II*, 1, 203 (1935).

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## Double Molecules in Gases

*Sir:* Possibly because the chemist is introduced to real gas behavior through the van der Waals equation, the presence of bound double molecules (as well as larger aggregates) in gases does not receive much attention in the literature. However, current statistical mechanical theories clearly point to such bound aggregates as a major source of the deviation from ideal gas behavior.<sup>1</sup>

The question that remains unanswered is under what conditions these associated species are more important to kinetic and spectroscopic events than simple colliding pairs of molecules. The importance of double molecules in termolecular reaction kinetics will be discussed in a later publication. Our present concern lies with the possibility of direct observation of these bound pairs by their characteristic electronic absorption spectra.

There are at least three spectroscopic events that require two molecules in close proximity: (1) charge-transfer, (2) simultaneous, and (3) induced transitions. They are easily recognized because the absorbance due to such transitions is proportional to the square of the molecular concentration. Though a number of bands with this property can be found in the literature, seldom has the temperature of the gas been varied to determine whether the absorbing species is a bound pair or a colliding pair. If it is a colliding pair, the integrated band intensity should remain the same or increase slightly as the temperature is raised. On the other hand, a bound pair should dissociate as the temperature is raised decreasing the absorption in the band. We have found an ultraviolet band of bromine which displays this latter type of behavior.

The uppermost curve in Figure 1 shows the absorption spectrum of bromine vapor (130 torr, 14°, 10-cm. path) between 1850 and 2500 Å. Figure 2 shows the linear relationship between the absorbance in the band and the square of the concentration, indicating that the transition involves two molecules. The lower curves in Figure 1 illustrate the effect of raising the temperature of a fixed amount of bromine vapor. It is clear that the peak at 2080 Å. is rapidly removed as the temperature is increased from 14 to 200°. Further increases in temperature beyond 200° have little effect on the absorption in this region.

It seems reasonable to assume that the portion of the band which is removed by heating the cell is due to bound double molecules and that there is an

(1) D. E. Stogryn and J. O. Hirschfelder, *J. Chem. Phys.*, 31, 1531 (1959).

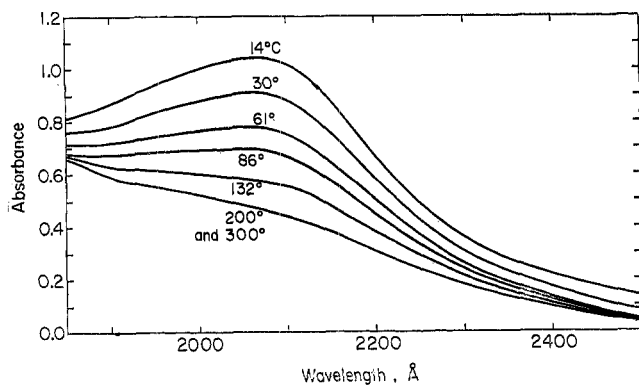


Figure 1. Ultraviolet absorption of bromine vapor. Path length, 10 cm.;  $[\text{Br}_2] = 10^{-2} M$ .

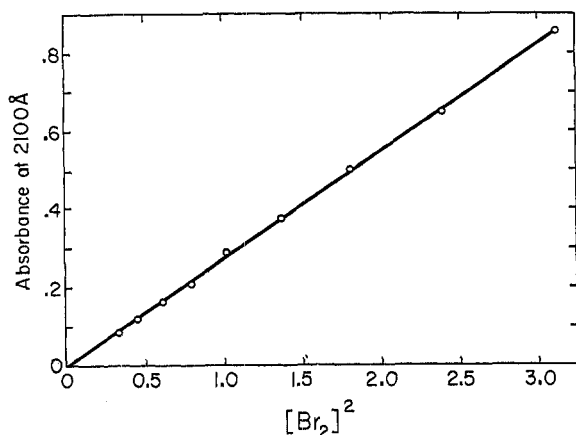


Figure 2. Relationship between  $[\text{Br}_2]^2$  and the absorbance at 2100 Å.

underlying absorption due to colliding pairs and/or the tail of a stronger band at 1600 Å. reported by Cordes and Sponer.<sup>2</sup> With this assumption the absorbance due only to double molecules can be obtained by subtraction. A plot of  $\log(A/T)$  against  $(1/T)$  can then be used to calculate the enthalpy change ( $\Delta H_2$ ) in the formation of double molecules. Such a plot is shown in Figure 3. From the slope at 25°  $\Delta H_2 = -2.6$  kcal. Hence, the bond energy  $E = -\Delta U = 2.0$  kcal.

Because of a paucity of *PVT* data for the halogens, it is not possible to compare our value of the double-

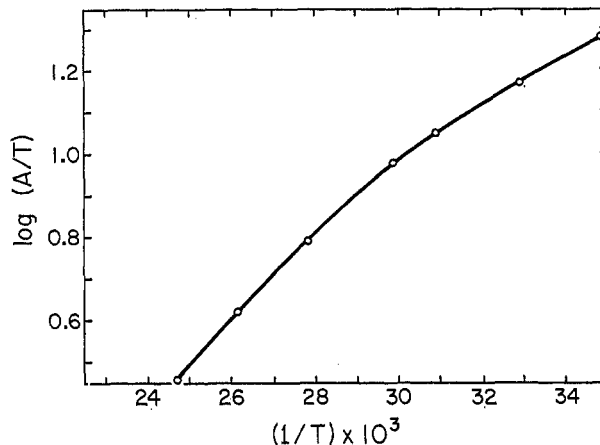


Figure 3.

molecule dissociation energy with that calculated from association theory.<sup>3</sup> However, the value is consistent with that obtained from *PVT* data for hydrocarbons with boiling points similar to bromine.<sup>4</sup>

Two recent communications provide the only additional direct evidence for bound (nonpolar) double molecules in gases. Watanabe and Welsh<sup>5</sup> have reported new absorption bands in hydrogen gas at 30°K. which they attribute to bound levels of  $(\text{H}_2)_2$ , and Robbins and Leckenby<sup>6</sup> have reported mass spectrometric evidence for appreciable concentrations of species such as  $\text{Ar}_2$ ,  $\text{Xe}_2$ ,  $(\text{N}_2)_2$ , and  $(\text{O}_2)_2$  in gases at 200 torr. There is little doubt that such species can be observed directly by techniques similar to those described in this paper since simultaneous, induced, or charge-transfer transition can be found for most molecules.

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(4) J. O. Hirschfelder, F. T. McClure, and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

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(6) E. J. Robbins and R. E. Leckenby, *Nature*, **206**, 1253 (1965).

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