ISOTOPE DEPENDENCE OF THE BREAKDOWN STRENGTH OF GASES*

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It has been found that while the highly nonuniform direct current breakdown voltages, V_s, of H_2 and NH_3 exceed, respectively, those of D_2 and ND_3, the V_s of CH_4 is substantially lower than that of CD_4. The former (direct) isotope effect may be attributed to the higher ionization coefficients for the deuterated species compared with the nondeuterated, and the latter (inverse) isotope effect may result from differences in the electron-impact-induced dissociation processes of the isotopic pairs of molecules.

We have measured the direct current (DC) breakdown strengths of H_2 and D_2 and NH_3 and ND_3 at 204 kPa and CH_4 and CD_4 at 102 kPa under highly nonuniform and quasi-uniform field conditions using, respectively, point-plane and sphere-sphere electrodes. The point electrode was a 0.5-cm-diameter rod with a 30° cone terminating into a hemispherical tip with a radius of 0.1 cm. The plane electrode had a diameter of 2.8 cm and a hemispherical edge with a radius of 0.3 cm. The sphere electrodes consisted of a pair of identical spheres of 0.476-cm radii. All electrodes were highly polished. For each set of data either new electrodes or used electrodes which were polished and cleaned were used. The results of our measurements are shown in Figs. 1, 2, and 3. The data points are the mean values of several measurements. The error bars represent ± one standard deviation. When no error bars are shown, these fall within the symbol size. For both geometries the field becomes progressively non-uniform with increasing electrode gap d.

The behavior of the V_s for the H_2/D_2 and NH_3/ND_3 pairs of molecules is similar. Both, for quasi-uniform and for highly nonuniform fields, the V_s of the deuterated species
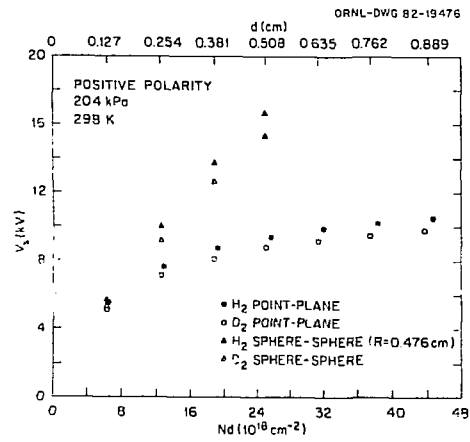

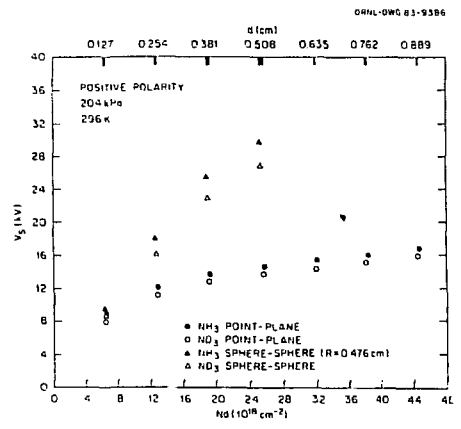Fig. 2. V_s versus Nd for NH_3 and ND_3.

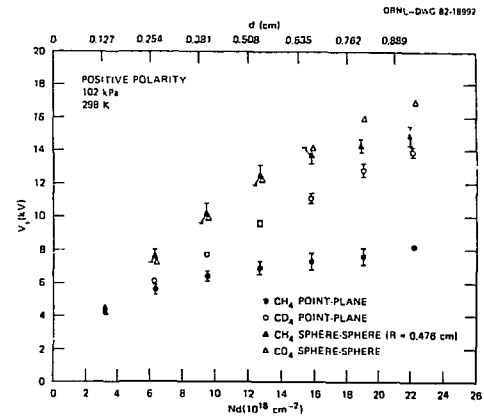
Fig. 3. V_s versus Nd for CH_4 and CD_4.

Fig. 1. V_s versus Nd for H_2 and D_2.

is lower. It also appears that the isotopic dependence of the V_s for both pairs of molecules is somewhat larger for the less nonuniform field. For the H_2/D_2 pair the available data on both the electron transport coefficients and the ionization processes show that the ionization coefficient α/N is higher for D_2 than for H_2. We, then, may attribute the observed direct isotope effect in V_s for H_2/D_2 (and by analogy for NH_3/ND_3) to the higher α/N for D_2 compared with H_2. For H_2 and D_2, $\alpha/N = \bar{\alpha}/N (\equiv (\alpha-\eta)/N)$ (η is the electron attachment coefficient) since for neither H_2 nor D_2 is electron attachment significant.[1]

In contrast to the behavior of the V_s for the H_2/D_2 and N_3/ND_3 pairs, a stronger and opposite (inverse) isotope effect is observed for the CH_4/CD_4 pair of

molecules. Although we are not aware of any high E/N (close to the limiting value of E/N) electron transport data for either CH$_4$ or CD$_4$, the low-E/N data on the Townsend energy factor[2] (= ratio of mean electron energy to the mean energy of the gas molecules) and the electron drift velocity[3] for CH$_4$ and CD$_4$ exhibit a similar isotope dependence to the H$_2$/D$_2$ data, and hence the V$_s$ ought to have been larger for CH$_4$ than for CD$_4$. Such a direct isotope effect may indeed be present; however, it appears to be overshadowed by an opposite effect responsible for the observed *inverse* isotopic behavior of V$_s$.

In an effort to rationalize the inverse isotope effect on V$_s$ we focused on the possible effects of electron-impact-induced molecular dissociation into neutral fragments (e$_{fast}$ + AX → A + X + e$_{slow}$). [Another process of interest in this connection--but which leads to ionization--is dissociative ionization (e$_{fast}$ + AX → A$^+$ + X + 2e).] If appreciable molecular dissociation by electron impact into neutral fragments occurs in the high-field region, and the fragments are produced with large amounts of kinetic energy enabling them--and the molecules to which they impart a fraction of their energy--to escape the high-field region, a *temporary local decrease* in N may result which will increase the local E/N value and enhance the processes that lead to the discharge development. To rationalize the V$_s$ data on H$_2$/D$_2$ and CH$_4$/CD$_4$ in highly nonuniform fields on the basis of this hypothesis, it is necessary to assume that this effect is more pronounced for CH$_4$/CD$_4$ than for H$_2$/D$_2$.

The cross section, σ_{diss}, for electron-impact-induced dissociation of CH$_4$ and H$_2$ into neutral fragments is shown in Fig. 4, where it is compared with the respective total ionization cross section σ_{iT}. It is seen that σ_{diss} for CH$_4$ is very large. There is also evidence (e.g., see Ref. 4) that the neutral fragments in the electron-impact-induced dissociation of CH$_4$ have considerable kinetic energy. (It should also be noticed that the dissociative ionization cross section for CH$_4$ is substantial.[7]) For H$_2$, on the other hand, σ_{diss} is smaller and the kinetic energies of the electron-impact-induced dissociation fragments seem[8,9] to be lower than those of CH$_4$/CD$_4$. For both pairs of molecules, H$_2$/D$_2$ and CH$_4$/CD$_4$, σ_{diss} is *larger for the lighter isotopic species*.[9,10]

Although it is difficult to assess quantitatively the effects on V$_s$ of the differences in the cross sections and kinetic energies of the dissociative products in H$_2$/D$_2$ and CH$_4$/CD$_4$, it seems possible that the larger cross section for dissociation (and perhaps also the larger kinetic energies of the dissociation fragments) for CH$_4$/CD$_4$ may lead to significant "microscopic expansion"[11] effects. If this is so, the differences between the V$_s$ of CH$_4$ and CD$_4$ can be ascribed to differences in the hydrodynamic behavior of the two isotopic gases in highly nonuniform fields resulting from the larger dissociation cross sections and larger speeds of the fragments for CH$_4$ compared with CD$_4$. Within this interpretation, *no inverse isotope effect should be detected in the V$_s$ of CH$_4$/CD$_4$ under uniform field conditions.* From the data on CH$_4$/CD$_4$ in
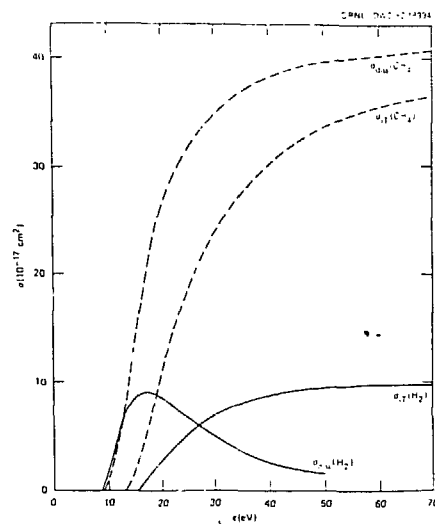

Fig. 4. σ_{diss} versus ε for CH$_4$ (Ref. 4) and H$_2$ (Ref. 5) and σ_{iT} versus ε for CH$_4$ and H$_2$ (Ref. 6).

Fig. 3 using sphere-sphere electrodes (quasi-uniform fields), it is indeed seen that the inverse isotope effect *disappeared* as long as the field was quasi-uniform; when (as d was increased) the field became gradually nonuniform, the inverse isotope effect began to set in (see Fig. 3). More work is needed to understand both types of isotope effects and is in progress.

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