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1. INTRODUCTION

Christophorou et al.[1] found that both the uniform and the nonuniform field direct current (dc) breakdown voltages (V_s) of H_2 exceed, respectively, those of D_2 for positive polarity. In contrast, they found that while for uniform fields CH_4 and CD_4 behave in a similar manner, the V_s of CD_4 exceeds that of CH_4 in nonuniform fields (dc; positive polarity). The isotopic dependence $V_s(H) > V_s(D)$ was termed[1] direct and that where $V_s(H) \lesssim V_s(D)$ inverse. Christophorou et al.[1] attributed the direct isotope effect to the larger ionization coefficients for the deuterated species compared with the nondeuterated and suggested that the inverse isotope effect may result from differences in the electron impact-induced dissociation processes of the isotopic pairs of molecules. In a later publication Christophorou et al.[2] reported that the dc positive polarity V_s of NH_3 and ND_3 behaves similarly to H_2/D_2.

In this paper we report: (1) the finding that the CH_4/CD_4 nonuniform field behavior is polarity dependent (i.e., the V_s of CD_4 is lower than the V_s of CH_4 for negative polarity which is just the opposite of that observed for positive polarity), (2) discuss the origins of the observed isotope effects and predict new isotopic dependences of V_s, and (3) report results on the V_s of H_2S and D_2S for negative polarity which confirm their predicted isotopic behavior.

2. DIRECT CURRENT BREAKDOWN STRENGTH

The positive polarity V_s data for the pairs of molecules H_2/D_2, CH_4/CD_4, and NH_3/ND_3 were reported earlier.[1,2] In Fig. 1 are presented our V_s measurements for CH_4/CD_4 for 106.67 kPa using dc negative polarity under conditions identical to those for positive polarity.[1] For any given pressure and gap length (which was varied in ascending and descending order), a minimum of ten voltage applications were made. The data presented in Fig. 1 are the average values of these breakdown voltages. The error is estimated to be ±2 to 5%.

Following the measurements in Refs. 1 and 2 and in Fig. 1 at Oak Ridge National Laboratory (ORNL), similar studies were initiated at the Laboratoire de Physique des Decharges (LPD). Preliminary measurements at LPD on H_2 and D_2 agree with those obtained at ORNL.[1,2] However, preliminary measurements on CH_4/CD_4, while confirming the existence of the observed isotopic effects reported in Refs. 1 and 2 and its polarity dependence (Refs. 1 and 2 and Fig. 1), indicate that the breakdown voltages measured at LPD are generally lower than those measured at ORNL and that the isotopic differences in the LPD data are smaller. These differences between the measurements at the two laboratories are under investigation and do not affect the discussion and conclusions in this paper.
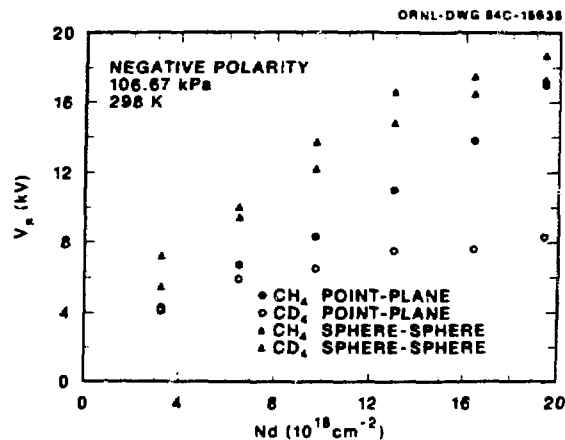
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Fig. 1. Negative polarity dc V_s versus Nd for CH_4 and CD_4 for 106.67 kPa.

3. ORIGINS AND CLASSIFICATION OF THE OBSERVED ISOTOPE EFFECTS; PREDICTION OF NEW ISOTOPIC DEPENDENCES OF V_s

The origins of the observed isotope effects and their polarity dependence in nonuniform fields are related to changes in the effective ionization coefficient $\bar{\alpha}/N$ and the changes in either or both the ionization, α/N, and the attachment, η/N, coefficients. We shall separate the isotopic pairs of molecules we studied into three groups: (1) nonelectronegative gases (where only changes in α/N are important); (2) weakly and moderately electronegative gases (where changes in α/N and/or η/N are important); and (3) strongly electronegative gases (where no isotopic dependence of V_s is expected since only η/N is important and does not show significant isotopic dependence, Section 3.3).

3.1. Nonelectronegative gases

The molecules H_2/D_2 belong to this category. As can be seen from Fig. 2, their electron attachment cross sections, $\sigma_a(\varepsilon)$, are small and lie at high energies. For these systems, then, we need to consider only the isotopic dependence of α/N to understand the isotopic dependence of V_s.

Besides the $\sigma_a(\varepsilon)$ in Fig. 2, we present in Fig. 3 the electron impact total ionization cross section $\sigma_{iT}(\varepsilon)$ and the α/N (as a function of the density-reduced electric field E/N) for H_2/D_2. The total electron impact ionization cross section $\sigma_{iT}(\varepsilon)$ and the total electron impact dissociation cross section $\sigma_{diss}(\varepsilon)$ are shown in Fig. 4 for H_2.

The lower values of V_s for D_2 for both uniform and nonuniform fields[1,2] can be attributed to the larger α/N values for D_2 compared with H_2. Two sources
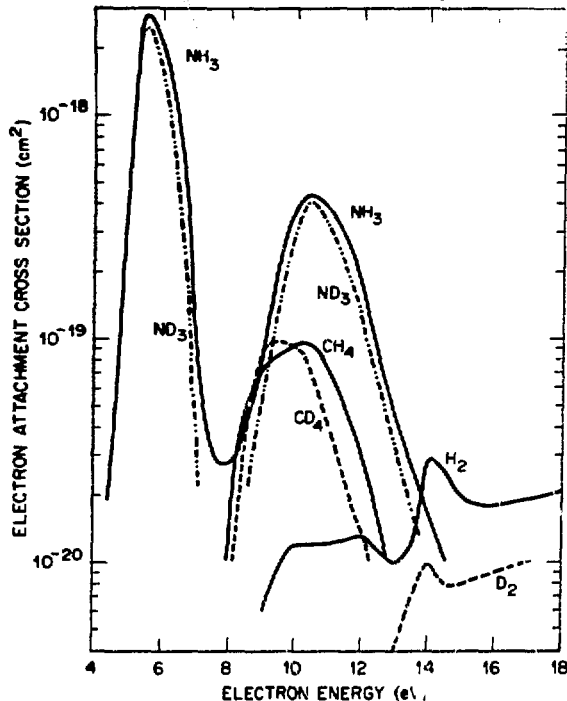
Fig. 2. Electron attachment cross section as a function of electron energy for NH_3/ND_3, CH_4/CD_4, and H_2/D_2 (see original references in [3]).

Fig. 4. σ_{iT} versus ε for H_2, CH_4, and NH_3; σ_{diss} versus ε for CH_4 and H_2 (see original references in [3]).
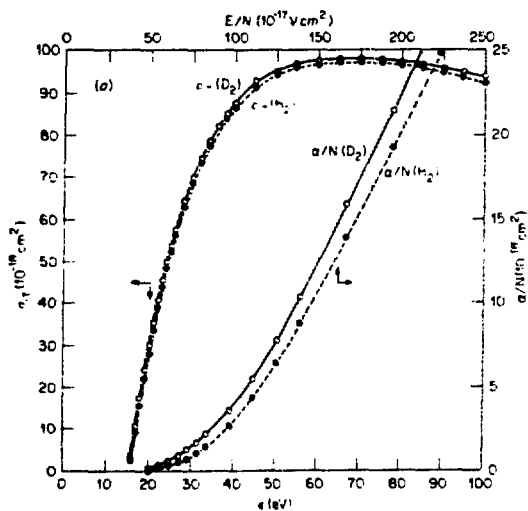

Fig. 3. $\sigma_{iT}(\varepsilon)$ and $\alpha/N(E/N)$ for H_2 and D_2 (see sources of data in [3]).

contributing to the larger values of α/N for D_2 compared with H_2 are: differences in $\sigma_{iT}(\varepsilon)$ and differences in the electron energy distribution function $f(\varepsilon,E/N)$. The former is especially significant when electron impact-induced dissociation into neutrals effectively competes with autoionization, while the latter may result from the isotopic dependence of the vibrational electron energy loss.

3.2. Weakly and moderately electronegative gases

In this category we have to consider $\bar{\sigma}/N$ (i.e., both α/N and η/N). We may distinguish three subgroups: (1) those isotopic species for which $\sigma_a(\varepsilon)$ is not strongly affected by the mass and is small, (2) those
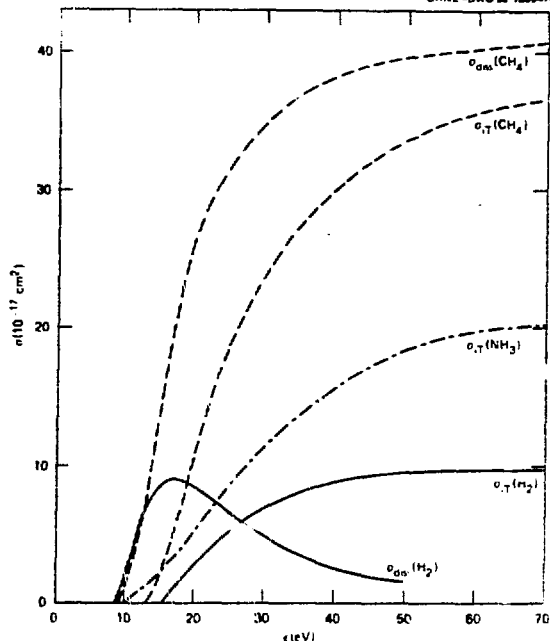
for which $\sigma_a(\varepsilon)$ is not strongly affected by the mass and is sizeable, and (3) those for which the magnitude of $\sigma_a(\varepsilon)$ is moderate and is strongly dependent on mass. The isotopic pairs CH_4/CD_4, NH_3/ND_3, and H_2S/D_2S are representative of (1), (2), and (3), respectively.

3.2.1. CH_4/CD_4

On the basis of the $\sigma_a(\varepsilon)$ data in Fig. 2, it seems reasonable to assume that $(\eta/N)_D \simeq (\eta/N)_H$ and small. We, therefore, attempt to understand the observed isotopic dependences of V_s for CH_4/CD_4 principally in terms of α/N.

The $\sigma_{iT}(\varepsilon)$ for CH_4 is shown in Fig. 4 and is seen to be smaller than $\sigma_{diss}(\varepsilon)$. While we know of no $\sigma_{iT}(\varepsilon)$ data for CD_4 at low ε, for high energy electrons there is virtually no difference in the $\sigma_{iT}(CD_4)$ and $\sigma_{iT}(CH_4)$. However, close to the ionization threshold, I, we would expect differences in the $\sigma_{iT}(\varepsilon)$ between CH_4 and CD_4 because (1) in this energy region a substantial portion of the ionization is indirect (i.e., via superexcitation) and (2) $\sigma_{diss}(\varepsilon)$ is large for the CH_4/CD_4 molecules. Indeed, Vroom and de Heer[4] found that dissociative excitation of CH_4 is ~20% larger than for CD_4. Hence, close to I the process

$$e + CH_4(CD_4) \rightarrow CH_4^*(CD_4^*) \xrightarrow{k_i} \text{ions}$$
$$\xrightarrow{k_\eta} \text{neutrals} \qquad (1)$$
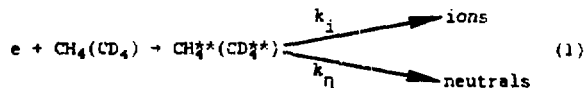
where $CH_4^*(CD_4^*)$ denote superexcited $CH_4(CD_4)$ molecules, introduces an isotope effect in α/N; because k_η is smaller for the heavier molecule CD_4.

$$(\alpha/N)_{CH_4} < (\alpha/N)_{CD_4} . \qquad (2)$$

The observed isotopic dependence of V_s for CH_4/CD_4 and its variation with polarity can be rationalized on the basis of (2).

3.2.1.1. Uniform field data

Here the value of E/N is always $\leq (E/N)_{lim}$ and hence only a small part of $f(\varepsilon, E/N)$ overlaps $\sigma_i(\varepsilon)$ at any value of E/N. While the values of α/N for $E/N \leq (E/N)_{lim}$ are small, the inequality (2) can account for the slightly higher V_s for CH_4 compared with CD_4.

3.2.1.2. Nonuniform field data

Under the present conditions of point-plane geometry, the $(V_s)_D > (V_s)_H$ for positive polarity[1,2] and the $(V_s)_D \lessgtr (V_s)_H$ for negative polarity (Fig. 1). For this electrode geometry the value, $(E/N)_{tip}$, of E/N at the tip of the point electrode is larger compared with the average, $(E/N)_{av}$ value of E/N at which the gap breaks down. The higher fields close to the tip of the point electrode would shift $f(\varepsilon, E/N)$ to higher energies compared with the rest of the gap, and hence reaction (1) would be more probable, making the difference $(\alpha/N)_D - (\alpha/N)_H$ larger close to the tip of the electrode compared with the rest of the gap. The finding, then, that $(V_s)_D > (V_s)_H$ for positive polarity can be rationalized as resulting from the better shielding of the positive electrode in the case of CD_4 because of the larger amount of homopolar (positive) charge compared with CH_4. The opposite behavior $[(V_s)_D < (V_s)_H]$ observed for negative polarity can also be rationalized on the basis of (2), since for negative polarity additional ionization (for CD_4) will decrease rather than increase V_s.

It is thus indicated that differences in σ_{diss} between CH_4 and CD_4 influence the value of α/N and, consequently, the space charge density in the high field region, accounting in this way for the observed differences and polarity dependence of the V_s of CH_4 and CD_4.

3.2.2. NH_3/ND_3

For this pair of molecules $(V_s)_{NH_3} > (V_s)_{ND_3}$ for both uniform and nonuniform fields.[1,2] This can be understood on the basis of the isotopic dependence of α/N and η/N. Since, as discussed above for H_2/D_2 and CH_4/CD_4, $(\alpha/N)_H < (\alpha/N)_D$ and since $(\eta/N)_H > (\eta/N)_D$ (Fig. 2), $(\bar{\alpha}/N)_H < (\bar{\alpha}/N)_D$. However, these differences are small and so is the resultant difference in $(V_s)_D$ and $(V_s)_H$. That the difference $(V_s)_D - (V_s)_H$ is somewhat smaller for nonuniform fields is again consistent with the expected changes in $\bar{\alpha}/N$: in the nonuniform field case $f(\varepsilon, E/N)$ shifts to higher energy compared with the uniform field and thus $(\eta/N)_H - (\eta/N)_D$ decreases more than $(\alpha/N)_D - (\alpha/N)_H$ increases.

3.2.3 H_2S/D_2S

If for a weakly electronegative pair of molecules $\sigma_a(\varepsilon)$ depends strongly on the mass, then large changes in η/N and thus $\bar{\alpha}/N$ for isotopic species are possible and consequently the V_s values of such isotopic species can be substantially different. Large isotopic dependences of $\sigma_a(\varepsilon)$—and thus η/N—are known to occur[5] when $\sigma_a(\varepsilon)$ exhibits a vertical onset behavior[5] which is usually the case when dissociative attachment proceeds via a negative ion state which is attractive, and dissociative attachment is then strongly influenced by the time it takes for the dissociation fragments to separate as opposed to the time of autodetachment.

Based on electron attachment and electron scattering data,[3,6] we selected the pair of molecules H_2S/D_2S to test the above hypothesis. Dissociative attachment to H_2S/D_2S produces[3,6] $HS^-(DS^-)$, $H^-(D^-)$, and S^- anions.

The cross section for H_2S and the ratio of the cross sections for the various fragment anions for H_2S and D_2S are shown in Fig. 5. It is seen that the isotopic dependence of $\sigma_a(\varepsilon)$ is large, especially for the most abundant fragment HS^- (DS^-).
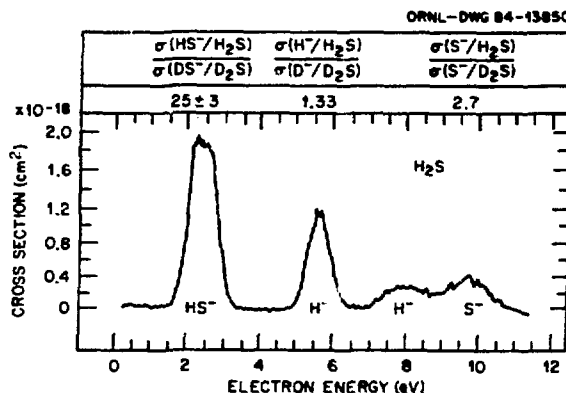

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Fig. 5. Dissociative attachment to H_2S producing HS^-, H^-, and S^- [7]. The peaks were identified with the predominant anions observed although the H^- peaks may contain some S^- ions (see original references in [3]). Ratios of the cross sections for the various fragments for H_2S and D_2S (inset).

In Fig. 6 are shown the V_s of H_2S and D_2S we measured for dc negative polarity using the same electrode geometries[1] (sphere-sphere and point-plane) as for the rest of the data. Although η/N versus $\langle\varepsilon\rangle$ have not been reported for either H_2S or D_2S, the fact that $(\sigma_a)_{H_2S} \gg (\sigma_a)_{D_2S}$ would lead one to expect $(\eta/N)_H > (\eta/N)_D$. Since moreover $(\alpha/N)_H \leq (\alpha/N)_D$ we conclude that $(\bar{\alpha}/N)_D > (\bar{\alpha}/N)_H$. Thus, the $V_s(H_2S)$ must be higher than the $V_s(D_2S)$. The experimental data shown in Fig. 6 amply demonstrate that this is so.

3.3. Strongly electronegative gases

No isotope effect is expected for positive or negative polarity for either uniform or nonuniform fields for such gases. Here the determining quantity is η/N, and it seems unlikely that an isotopic difference can introduce large enough changes in η/N to affect V_s. Strongly electron attaching gases are, as a rule, polyatomic and thus the difference—if any—between the $f(\varepsilon, E/N)$ of isotopic species is small. Hence, for $(\eta/N)_H$ to be different from the $(\eta/N)_D$, a large difference between $(\sigma_a)_H$ and $(\sigma_a)_D$ must exist and this is unlikely[6] for strongly electronegative gases.

4. CONCLUSION

The results presented in this paper suggest that the isotopic dependences of the V_s of gases are apparently of more general occurrence than hitherto recognized; they can be rationalized and indeed predicted from basic data on electron-collision cross sections.

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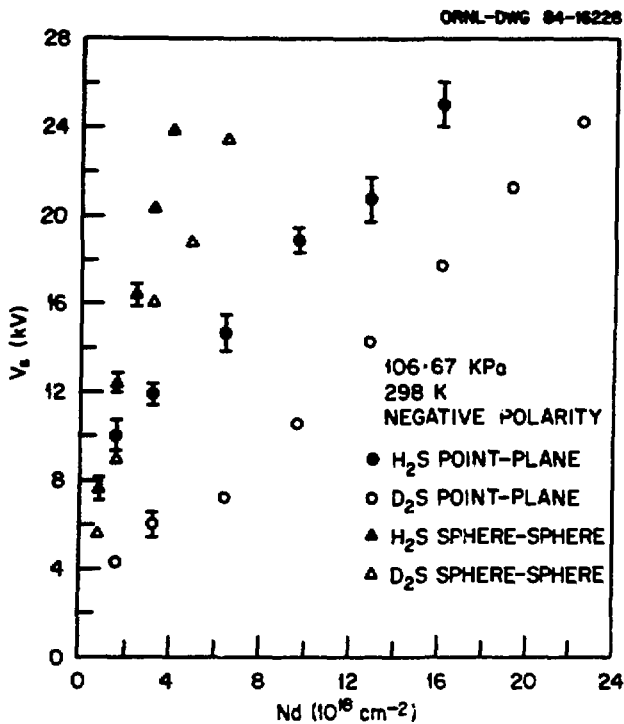7. Azria, R., M. Tronc, and S. Goursaud, 1972, **J. Chem. Phys. 56**, 4234.

Fig. 6. Negative polarity dc V_s versus Nd for H_2S and D_2S at 106.67 kPa (similar results were obtained for a pressure of 156.68 kPa).

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