

Negative-Ion Formation in H₂O and D₂O†

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The electron swarm-beam technique was employed to determine the dissociative attachment cross sections for H₂O and D₂O. The formation of H⁻ from H₂O peaked at an energy, ϵ_{\max} , equal to 6.5 ± 0.1 eV, and the cross section $\sigma_c(\epsilon_{\max})$ for the process at ϵ_{\max} was found to be 6.9×10^{-18} cm². For D⁻ from D₂O, ϵ_{\max} was 6.5 ± 0.1 eV and $\sigma_c(\epsilon_{\max})$ was 5.2×10^{-18} cm². Data on the formation of O⁻ from H₂O and D₂O are also presented. Interesting isotope effects in the cross section for the formation of H⁻ from H₂O and D⁻ from D₂O, and the relative ion yields of the three O⁻ peaks from H₂O and D₂O were observed and are discussed in relation to existing theories for dissociative electron attachment. Data are also reported for ion-molecule reactions occurring in H₂O and in H₂O-O₂ mixtures.

I. INTRODUCTION

THE formation of negative ions in water vapor has been the subject of many investigations.¹⁻¹⁰ Buchel'nikova⁶ and Schulz⁸ have performed total-ionization experiments on the formation of negative ions in water vapor and their results, combined with mass-spectroscopic measurements, have shown that the principal negative ion formed by electron impact in water is H⁻, the negative atomic oxygen ions being about ten times less abundant (the main O⁻ peak occurs in the vicinity of 11.5 eV). Buchel'nikova⁶ has also determined the cross section for the formation of H⁻ from H₂O. Energy integrated cross sections for the formation of H⁻ from H₂O and D⁻ from D₂O were obtained by Hurst *et al.*^{11,12} In this article we report electron-capture cross sections for the formation of H⁻ from H₂O and D⁻ from D₂O, determined by the swarm-beam method,¹³ and we investigate the isotope effects in the formation of H⁻ from H₂O and D⁻ from D₂O, and O⁻ from H₂O and D₂O.

II. EXPERIMENTAL METHOD

The electron-capture cross sections as a function of energy, $\sigma_c(\epsilon)$, were determined by the swarm-beam

method described previously.^{13,14} The swarm-beam technique has been established¹³⁻¹⁶ as a means of measuring $\sigma_c(\epsilon)$ (see Sec. III of this article) and of calibrating the electron-energy scale.

The absolute rates for dissociative electron capture by H₂O and D₂O were taken from earlier publications by Hurst, O'Kelly, and Bortner,¹¹ and by Stockdale and Hurst.¹² The D₂O sample used in the swarm experiments of Stockdale and Hurst¹² was mass-analyzed in the present work and found to contain less than 2% of H₂O as an impurity, but no other impurities were detected.

In our beam experiments the approximately zero¹⁷ electron-energy resonance capture in SF₆ was employed to obtain a first estimate of the electron-energy scale. Special attention was given to avoid loss of H⁻ ions (because of the considerable kinetic energy they possess) to the walls of the ion source before they can be pulsed into the mass-analysis section of the mass spectrometer. Applying the backing-plate pulse less than 1 μ sec after application of the electron gate pulse, the H⁻ ion current yield as a function of energy was similar to that of the total ionization experiments.^{6,8} The ratio of the second H⁻ peak to the first differs somewhat from the total ionization experiments of Refs. 6 and 8, which indicates that ion-discrimination effects may be suppressing the higher energy H⁻ peak in the present experiment. However, as shown later in the paper, the slight difference in the H⁻ peaks at 6.8 eV does not appreciably alter the maximum cross section.

Because of the small abundance of O⁻ as compared to H⁻ and the fact that the major O⁻ ion current occurs at electron energies which are well above the mean energy of the electron swarm, the capture rates measured by the electron swarm method^{11,12} are taken to be those for H⁻ from H₂O. It is estimated from the electron distribution functions tabulated by Ritchie and

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¹ W. N. Lozier, *Phys. Rev.* **36**, 1417 (1930).

² M. M. Mann, A. Hustrulid, and J. T. Tate, *Phys. Rev.* **58**, 340 (1940).

³ B. Cox, Ph.D. thesis, University of Liverpool, 1953 (unpublished).

⁴ E. E. Muschlitz, Jr., and T. L. Bailey, *J. Phys. Chem.* **60**, 681 (1956).

⁵ E. E. Muschlitz, Jr., *J. Appl. Phys.* **28**, 1414 (1957).

⁶ I. S. Buchel'nikova, *Zh. Eksperim. i Teor. Fiz.* **35**, 1119 (1958) [English transl.: *Soviet Phys.—JETP* **8**, 783 (1959)].

⁷ M. Cottin, *J. Chem. Phys.* **56**, 1024 (1959).

⁸ G. J. Schulz, *J. Chem. Phys.* **33**, 1661 (1960).

⁹ B. C. DeSouza and J. H. Green, *Nature* **203**, 1165 (1964).

¹⁰ F. H. Dorman, *J. Chem. Phys.* **44**, 3856 (1966).

¹¹ G. S. Hurst, L. B. O'Kelly, and T. E. Bortner, *Phys. Rev.* **123**, 1715 (1961).

¹² J. A. Stockdale and G. S. Hurst, *J. Chem. Phys.* **41**, 255 (1964).

¹³ L. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.* **43**, 4274 (1965).

¹⁴ L. G. Christophorou, R. N. Compton, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.* **45**, 536 (1966).

¹⁵ R. N. Compton, G. S. Hurst, L. G. Christophorou, and P. W. Reinhardt, Oak Ridge National Laboratory Report No. ORNL-TM-1409, 1966 (unpublished).

¹⁶ R. N. Compton and P. W. Reinhardt (to be published).

¹⁷ W. M. Hickam and R. E. Fox, *J. Chem. Phys.* **25**, 642 (1956).

Whitesides¹⁸ that the three O⁻ peaks (see Fig. 4) contribute less than 3% of the total capture rate measured over the range of E/P covered in the swarm experiments.

The swarm experimental rates^{11,12} and the rates calculated from our electron beam experiments (after optimum translation)¹³ are plotted as a function of E/P in Fig. 1 for H₂O and D₂O. A positive energy shift of 0.3 eV for the case of H₂O and 0.5 eV for the case of D₂O was required to bring the experimental and calculated capture rates into agreement. The resulting energy scale agreed well with the experiments of Buchel'nikova⁶ and Schulz.⁸ The energy scale is also found to be consistent with the experiments of Buchel'nikova⁶ and Schulz.⁸ The energy scale is also found to be consistent with recent electron-impact-excitation experiments¹⁶ in H₂O and D₂O. When the total ionization curve of Schulz⁸ was treated with the swarm-beam technique, no energy shift was required

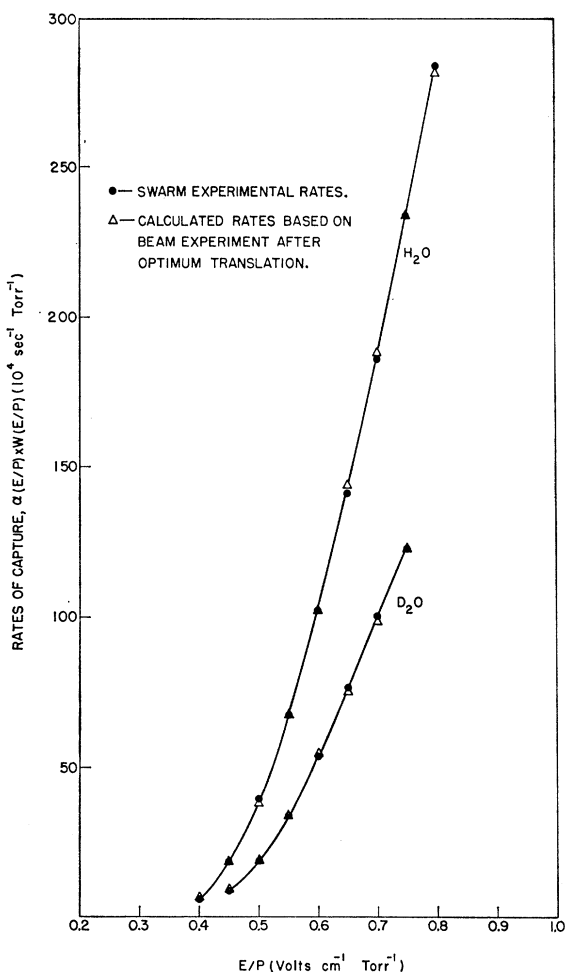


FIG. 1. Experimental and calculated rates of capture versus E/P for water and heavy water, for trial functions based on beam experiments.

¹⁸ R. H. Ritchie and G. E. Whitesides, Oak Ridge National Laboratory Report No. ORNL-3081, 1961 (unpublished).

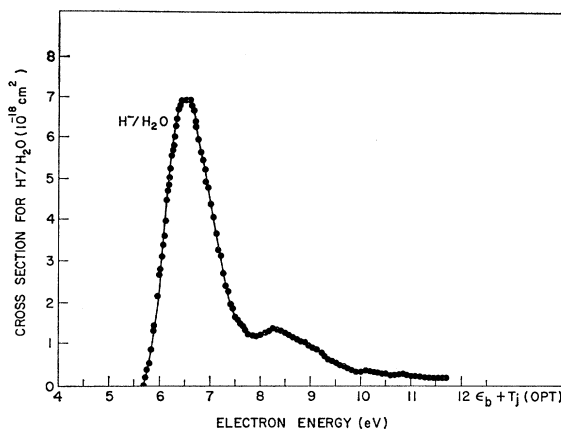


FIG. 2. Electron-capture cross section as a function of energy. Atomic-hydrogen negative ions from water.

to obtain agreement with the swarm capture rates.^{11,12} The maximum value $\sigma_c(\epsilon_{\text{max}})$ of $\sigma_c(\epsilon)$ as obtained from Schulz's beam data⁸ (swarm-beam combination)¹³ agreed to within 10% with our results.

III. RESULTS

A. Cross Sections for the Formation of H⁻ from H₂O and D⁻ from D₂O

The capture cross sections for the production of H⁻ from H₂O and D⁻ from D₂O are presented in Figs. 2 and 3, respectively. For both H⁻ from H₂O and D⁻ from D₂O, $\sigma_c(\epsilon)$ peaks at 6.5 ± 0.1 eV. A summary of the present study of H₂O in comparison with the results of others is compiled in Table I. The cross section reported by Buchel'nikova⁶ is about 30% lower than our value. It is interesting to note that this is approximately the same difference observed in the comparison of our value and that of Buchel'nikova⁶ for the cross section of O⁻ from O₂.¹³ However, the energy-integrated cross

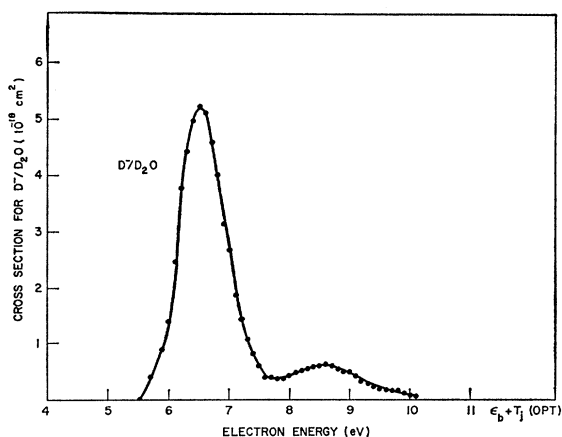


FIG. 3. Electron-capture cross section as a function of energy. Deuterium negative ions from heavy water.

TABLE I. Data for the production of H⁻ and O⁻ from H₂O; D⁻ and O⁻ from D₂O.

Reference	Probable process	Onset (eV)	Position of maximum (eV)	$\sigma_b(\text{max})$ (cm ²)	$\int \sigma(\epsilon) d\epsilon$ (cm ² eV)
Cox ^a	H ⁻ +OH	5.6 ± 0.5			
	H ⁻ +O+H				
Cottin ^b	O ⁻ +H ₂	7.5 ± 0.3			
	H ⁻ +OH	4.8 ± 0.2	6.0±0.2		
	H ⁻ +O+H		8.0±0.2		
	O ⁻ +...	7.4 ± 0.3	9.15		
Mann, Hustrulid, and Tate ^c	O ⁻ +...	5.6 ± 0.5	11.25		
	H ⁻ +OH		7.1		
	H ⁻ +O+H	7.5 ± 0.3	8.9		
	O ⁻ +...		8.2		
	O ⁻ +...		11.1		
Lozier ^d	O ⁻ +...		12.8		
	H ⁻ +OH		6.8		
Schulz ^e	H ⁻ +O+H	5.6 ± 0.1	8.8		
	H ⁻ +OH		6.5±0.1		
	H ⁻ (?)+OH		8.5±0.1		
Buchel'nikova ^f	O ⁻ +...	5.45±0.09	~12		
	H ⁻ +OH		6.4±0.1	(4.8±1.5)×10 ⁻¹⁸	6.5×10 ⁻¹⁸
Dorman ^g	H ⁻ (?)+OH		8.6±0.1	(1.3±0.1)×10 ⁻¹⁸	
	H ⁻ +OH		6.7±0.2		
	H ⁻ +OH		8.8±0.2		
	O ⁻ +H ₂		6.6±0.2		
	O ⁻ +...		8.9±0.2		
	O ⁻ +...		11.4±0.2		
Present work	H ⁻ +OH	5.7 ± 0.2	6.5±0.1	6.9 × 10 ⁻¹⁸	6.6×10 ⁻¹⁸
	H ⁻ +OH		8.6±0.2	1.3 × 10 ⁻¹⁸	
	O ⁻ +H ₂	4.9 ± 0.2	6.9±0.1		
	O ⁻ +...	7.8 ± 0.2	8.9±0.1		
Present work	O ⁻ +...		11.4±0.1		
	D ⁻ +OD	5.7 ± 0.2	6.5±0.1	5.2 × 10 ⁻¹⁸	3.9×10 ⁻¹⁸
	D ⁻ +OD		8.6±0.2	0.6 × 10 ⁻¹⁸	
	O ⁻ +D ₂	5.0 ± 0.2	7.0±0.1		
	O ⁻ +...	7.7 ± 0.2	9.0±0.1		
O ⁻ +...	11.8±0.1				

^a B. C. Cox, Ph.D. thesis, University of Liverpool, 1953 (unpublished).

^b M. Cottin, J. Chem. Phys. **56**, 1024 (1959).

^c M. M. Mann, A. Hustrulid, and J. T. Tate, Phys. Rev. **58**, 340 (1940).

^d W. W. Lozier, Phys. Rev. **36**, 1417 (1930).

^e G. J. Schulz, J. Chem. Phys. **33**, 1661 (1960).

^f I. S. Buchel'nikova, Zh. Eksperim. i Teor. Fiz. **35**, 1119 (1958) [English transl.: Soviet Phys.—JETP **8**, 783 (1959)].

^g F. H. Dorman, J. Chem. Phys. **44**, 3856 (1966).

section $\int_0^\infty \sigma_c(\epsilon) d\epsilon$ for H⁻ from H₂O as obtained from Fig. 2 is 6.6×10^{-18} cm² eV and compares favorably with the value of 6.5×10^{-18} cm² eV reported in the experiment of Buchel'nikova.⁶ [$\int_0^\infty \sigma_c(\epsilon) d\epsilon$ for O⁻ from O₂ was also the same for the two experiments.^{13,15}] It, therefore, appears that the slight discrepancy between the cross sections reported in the present work and those of Ref. 6 can be accounted for by a narrower electron-energy resolution in the present experiment.

B. Isotope Effects

Isotope effects were discovered (i) in the magnitude and width of $\sigma_c(\epsilon)$ for the formation of H⁻ from H₂O and D⁻ from D₂O and (ii) in the production of O⁻ from H₂O and D₂O.

(i) *H⁻ from H₂O and D⁻ from D₂O.* Data for the production of H⁻ from H₂O and D⁻ from D₂O are presented in Table I. The width of the D⁻ resonance at half-maximum was approximately 0.3 eV narrower than the H⁻ resonance (the width of the electron beam was approximately the same in the two measurements). This result is to be expected since the square of the

ground-state vibrational wave function for the D—OD motion is narrower than that of the H—OH motion. If one makes the often-invoked assumption that the yield of negative ions as a function of electron energy is a reflection of the square of the ground-vibrational-state wave function upon the potential energy curve of the negative ion, then a theoretical width to the ion current curves can be determined. If the H—OH and D—OD system is treated as a "diatomic" harmonic oscillator and the slope of the negative-ion potential curve in the Franck-Condon region is inferred from the cross-section curves in Figs. 2 and 3, the D⁻ ion current curve is ~0.25 eV narrower than the H⁻ ion current curve. This agrees well with the measured value of 0.3 eV.

The ratio of the D⁻ to the H⁻ cross section at the maximum was 0.75 and the corresponding ratio for the energy-integrated cross sections was 0.60. The swarm experiments of Hurst *et al.*^{11,12} gave energy-integrated cross sections for H⁻ from H₂O and D⁻ from D₂O equal to 7.7×10^{-18} cm² eV and 4.6×10^{-18} cm² eV, respectively. They obtained the integrated cross sections

from the swarm measurements by representing the microscopic cross section by a δ function at approximately 6.5 eV. Both of the values obtained in this manner are 14% higher than the integrated cross sections reported in the present work. The ratios of the integrated cross sections, however, are identical (~ 0.60).

(ii) O^- from H_2O and D_2O . Figure 4 shows a comparison of the two O^- ion current yields as a function of energy. The two curves exhibiting three characteristic peaks (see also Table I) were normalized at the second maximum. The calibration of the electron-energy scale was achieved by use of the H^- and D^- maxima. The positions of the three peaks are in good agreement with the experiments of Dorman,¹⁰ but do not compare favorably with the results of Melton¹⁹ and the others in Table I. For O^- from H_2O the peak at ~ 7 eV was not observed in the study by Cottin,⁷ but was clearly presented in the experiments of Mann *et al.*,² Cox,³ Dorman,¹⁰ and Melton.¹⁹ This peak may be due to oxygen impurities in the water sample. However, the ratio of this peak to the maximum (at ~ 11.5 eV) is approximately the same in the five experiments performed, and the possibility that the same percentage of oxygen was present in the five experiments seems unlikely. The position of the lowest peak is also significantly different from that for O^- from O_2 .¹³ The relative magnitudes of the three O^- peaks from H_2O were in good agreement with the measurements of Refs. 2, 10, and 19, but Cox³ observed the third peak to be smaller than the second. The marked differences in the shape of the O^- curves in Fig. 4 and those of Cox³ cannot be attributed to ion-discrimination effects which occur in our ion source. Ion discrimination due to kinetic energy is not believed to be occurring since increase of the residence time of the O^- ions in the mass spectrometer

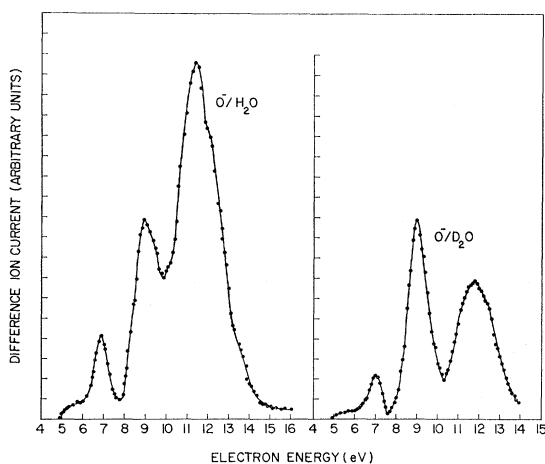


FIG. 4. Atomic-oxygen negative ions from water and heavy water.

¹⁹ C. E. Melton, in *Mass Spectrometry of Organic Ions*, edited by F. W. McLafferty (Academic Press Inc., New York, 1963), p. 192.

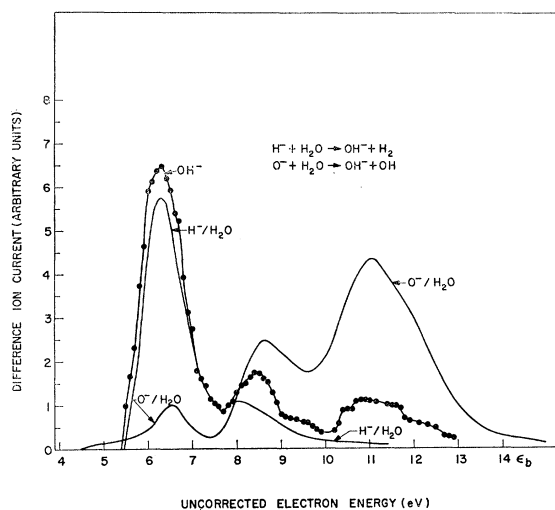


FIG. 5. Hydroxyl negative ions produced by ion-molecule reactions in water.

did not change the shape or relative magnitude of the O^- peaks. Also, instrumental effects such as ion source conditions cannot be responsible for the isotope effects observed in Fig. 4, since the shape of the current curves did not change when the backing system of the mass spectrometer was arranged so that H_2O or D_2O could be alternately introduced into the mass spectrometer under identical ion source conditions (i.e., pressure, pusher plate voltage, electron current, magnet position, ion focusing conditions, etc.). The ratio of the three O^- peaks from H_2O , starting with the peak at low energy were 0.42:1:1.8, and the ratio of the corresponding O^- peaks from D_2O were 0.22:1:0.7. Thus, the ratio of the ~ 11.5 -eV peak to that at ~ 9 eV for D_2O is significantly smaller than the corresponding ratio for H_2O . Such isotope effects have not been observed previously, but are to be expected from theoretical considerations (see Sec. IV).

C. Ion-Molecule Reactions in H_2O and H_2O-O_2 Mixtures

Negative hydroxyl ions are not observed in electron bombardment of water vapor at low pressures ($\sim 10^{-6}$ Torr) for electron energies below 15 eV. However, at higher pressures OH^- becomes the most abundant ion. The experiments discussed in Refs. 4, 5, and 7 showed that OH^- resulted from ion-molecule reactions involving H^- (and possibly O^-) with H_2O . Figure 5 indicates that the OH^- peaks correlate with the appearance of H^- and O^- . A plot of $\ln(OH^-)$ versus $\ln P(H_2O)$ yielded a slope of 2 over the pressure range from 10^{-5} to 10^{-3} Torr, which is expected for ion-molecule reactions. Furthermore, the OH^- ion current increased linearly with the time delay between the electron gate pulse and the ion-pusher pulse. Unfortunately, the effect of diffusion of H^- to the walls of the mass spectrometer did not

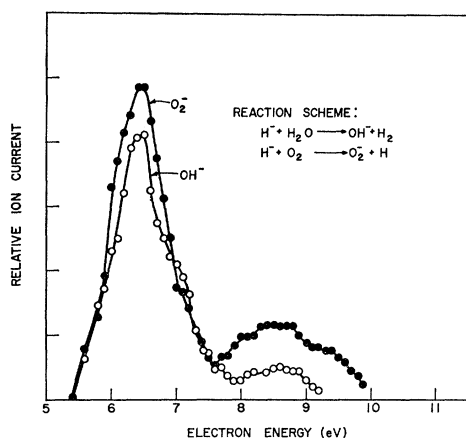
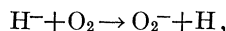


FIG. 6. Ion-molecule reaction in water-oxygen mixtures.

allow a measurement of the rate constant for the reaction.

Ion-molecule reactions occurring in $\text{H}_2\text{O}-\text{O}_2$ mixtures were also studied. Wobschall, Graham, and Malone²⁰ have observed O_2^- formed by ion-molecule reactions in $\text{H}_2\text{O}-\text{O}_2$ mixtures. The O_2^- ion current reported in Ref. 20 also exhibited a second maximum at higher energy which correlated with the appearance of H_2O^- . Our data on the formation of O_2^- in Fig. 6, however, shows that the two O_2^- peaks correspond exactly to the two OH^- (and consequently H^-) ion current peaks.²¹ Furthermore, no H_2O^- ions were detected in the energy region reported by Ref. 20.

The existence of the charge-transfer reaction,



requires²⁰ that either the electron affinity of O_2 is larger than that of H or that the kinetic energy of the separating $\text{O}_2^- - \text{H}$ system decreases over that of the $\text{H}^- - \text{O}_2$ system.

IV. DISCUSSION

Holstein²² discussed a phenomenological description of electron-capture reactions of the type $e + AB \rightarrow A + B^-$. The dissociative attachment cross section was represented as a product of the cross section for the formation of AB^- , σ_0 , times the probability, e^{-T_s/T_a} , that the ion will dissociate into a negative ion and a neutral without autoionization, i.e.,

$$\sigma_e = \sigma_0 e^{-T_s/T_a}, \quad (1)$$

where T_s is the time required for the ion and the neutral to separate to the crossing point of the AB and AB^- curves, and T_a is the auto-ionization lifetime. Equation

²⁰ D. Wobschall, J. R. Graham, Jr., and D. P. Malone, *J. Chem. Phys.* **42**, 3955 (1965).

²¹ The fact that the OH^- ions are not the precursors of the O_2^- current is evidenced by the linear dependence of the O_2^- ion current on the H_2O pressure (Ref. 20); thus they postulate the reaction sequence $\text{H}^- + \text{O}_2 \rightarrow \text{O}_2^- + \text{H}$.

²² T. Holstein, *Phys. Rev.* **84**, 1073 (1951).

(1) is the simplest interpretation of the more detailed resonance formalism derived by Bardsley, Herzenberg, and Mandl²³ and O'Malley.²⁴

Bloch and Bradbury²⁵ and Massey²⁶ have discussed electron capture and argued that the influence of the kinetic energy of the nuclei on the electronic wave functions gives rise to transitions which result in electron capture. Similarly, Chen²⁷ has presented a distorted wave method for calculating dissociative attachment cross sections by employing the kinetic-energy operator as the perturbing term in the Hamiltonian. More recently, Chen²⁸ has presented an exact description of dissociative attachment reactions which includes the adiabatic terms of Refs. 23 and 24 and the nonadiabatic terms discussed in Refs. 25–27.

It is difficult to treat our experimental results within the framework of the existing theories in a rigorous and unambiguous fashion. The complexity of the mechanisms of electron attachment is exemplified by the recent experiments of Rapp, Sharp, and Briglia²⁹ and Schulz and Asundi³⁰ where a large isotope effect was observed in the formation of negative ions from H_2 and D_2 and by the experiments of Fite, Brackmann, and Henderson³¹ where a large temperature dependence was observed in the formation of O^- from O_2 . We will, however, discuss briefly in the following sections the isotope effects observed in our experiments with respect to Eq. (1) and the simplest interpretation of the theoretical work in Ref. 27.

A. Auto-ionization Lifetime for $(\text{H}_2\text{O}^-)^*$

The isotope effects presented in Figs. 2 and 3 can be reconciled from Eq. (1) by choosing the proper auto-ionization lifetime for $(\text{H}_2\text{O}^-)^*$. T_a for $(\text{H}_2\text{O}^-)^*$ can be calculated from our results if we assume: (i) that the only difference in σ_0 for H_2O and D_2O at $\sigma_e(\epsilon_{\text{max}})$ is the effect of the square of the ground-state-vibrational wave function, i.e.,

$$(\sigma_0)_{\text{D}_2\text{O}} / (\sigma_0)_{\text{H}_2\text{O}} = 1.18, \quad (2)$$

²³ J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 415.

²⁴ T. F. O'Malley, in *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965*, edited by L. Kerwin and W. Fite (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 97; Technical Memorandum 344, Defence Research Corporation, Santa Barbara, California (unpublished); T. F. O'Malley, *Phys. Rev.* **150**, 14 (1966).

²⁵ F. Bloch and N. E. Bradbury, *Phys. Rev.* **48**, 689 (1935).

²⁶ H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1950), 2nd ed.

²⁷ J. C. Y. Chen, *Phys. Rev.* **129**, 202 (1963).

²⁸ J. C. Y. Chen, *Phys. Rev.* **148**, 66 (1966).

²⁹ D. Rapp, T. E. Sharp, and D. D. Briglia, *Phys. Rev. Letters* **14**, 533 (1965).

³⁰ G. J. Schulz and R. K. Asundi, *Phys. Rev. Letters* **15**, 946 (1965).

³¹ W. L. Fite, R. T. Brackmann, and W. R. Henderson, in *Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965*, edited by L. Kerwin and W. Fite (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 100.

and (ii) that T_a for (H₂O)⁻* and (D₂O)⁻* is essentially the same (i.e., assume no isotope effect in auto-ionization). Under these assumptions T_a is found to be 0.85 times the time required for the H⁻-OH system to separate to the crossing point of the H₂O and (H₂O)⁻* curves.

An approximate time of separation T_s can be calculated by assuming that the interaction potential between H⁻ and OH follows a $1/R^2$ law³² at small internuclear separations, i.e.,

$$V(R) = 1.96/R^2 + 4.35 \text{ eV.} \quad (3)$$

The numerical parameters appearing in Eq. (3) were chosen to approximate the potential curve of the negative ion in the Frank-Condon region, which is inferred from Fig. 2, and to give the proper asymptotic limits. The neutral and negative-ion curves were taken to cross at 2.0 Å which results in a value of $(T_s)_{\text{H-OH}}$ of approximately 2.5×10^{-14} sec. Thus, the auto-ionization lifetime becomes $\sim 2.1 \times 10^{-14}$ sec.

The above discussion merely shows that the observed isotope effect can be explained on the basis of auto-ionization prior to dissociation. This statement is not unique, however, since the assumption involving Eq. (2) may be in serious error allowing the isotope effect to be contained in the ratio $(\sigma_0)_{\text{D}_2\text{O}}/(\sigma_0)_{\text{H}_2\text{O}}$.

B. Isotope Effect in the Production of H⁻ from H₂O and D₂O

In Sec. A we invoked the isotope dependence of the probability of auto-ionization to account for the observed isotope effects in the magnitude of the dissociative electron-capture resonances. In this section we will show that the isotope effects can be explained in a much simpler manner without considering auto-ionization. From first-order perturbation theory³³ the cross section for attachment is given by

$$\sigma_c = \frac{m\mu L^6}{4\pi^2 \hbar^4} \frac{k_f}{k_i} |\langle \mathcal{H}'_{if} \rangle|^2, \quad (4)$$

where m is the mass of the electron, μ is the reduced mass of the dissociating particles, k_i and k_f are the amplitudes of the initial and final propagation vectors, respectively, and \mathcal{H}'_{if} is the perturbation operator (i.e., kinetic-energy operator). The wave functions are taken to obey periodic boundary conditions at the walls of a box whose sides are of length L . Now since

$$\langle \mathcal{H}'_{if} \rangle = \left\langle \psi_f \left| -\frac{\hbar^2}{2\mu} \nabla_R^2 \right| \psi_i \right\rangle, \quad (5)$$

the attachment cross section [Eq. (4)] is proportional to $\mu^{-1/2} |\langle \psi_f | \nabla_R^2 | \psi_i \rangle|^2$. Therefore, the ratio of the cross

section for D⁻ from D₂O to H⁻ from H₂O becomes

$$\frac{\sigma_{(\text{D}^-/\text{D}_2\text{O})}}{\sigma_{(\text{H}^-/\text{H}_2\text{O})}} = \left[\frac{\mu_{(\text{H}^- - \text{OH})}}{\mu_{(\text{D}^- - \text{OD})}} \right]^{1/2} \frac{|\langle \psi_f | \nabla_R^2 | \psi_i \rangle|^2_{\text{D}_2\text{O}^2}}{|\langle \psi_f | \nabla_R^2 | \psi_i \rangle|^2_{\text{H}_2\text{O}^2}}, \quad (6)$$

where we have approximated the ratio of the velocities of separation to be equal to the square root of the inverse ratio of the reduced masses. Experimentally we find that $\sigma_{(\text{D}^-/\text{D}_2\text{O})}/\sigma_{(\text{H}^-/\text{H}_2\text{O})}$ is numerically equal to $[\mu_{(\text{H}^- - \text{OH})}/\mu_{(\text{D}^- - \text{OD})}]^{1/2}$ which indicates that $|\langle \psi_f | \nabla_R^2 | \psi_i \rangle|$ is approximately the same for D₂O and H₂O.

In conclusion, either of the simple theories, described in Secs. IVA and IVB, can account for the observed isotope effect in the magnitude of the electron-capture cross sections.

C. Isotope Effect in the Production of O⁻ from H₂O and D₂O

The isotope effect shown in Fig. 4 can be justified by assuming proper auto-ionization rates to the three negative-ion states or by assuming the proper overlap integrals in Eq. (4). Certainly, the same relative heights for the O⁻ peaks would not be expected. Also, the production of O⁻ from H₂O and D₂O might be in competition with the formation of H⁻ and D⁻ at ~ 6.5 eV and ~ 9 eV (see discussion by Fayard³³) which could alter the relative heights of the three O⁻ peaks. Such a competition would not contribute much to a change in the relative cross sections for the production of H⁻ and D⁻ since the O⁻ peaks are much smaller. However, the heights of the O⁻ peaks might be greatly affected.

D. Associative-Detachment Cross Sections

Cross sections for electron-capture reactions ($e + AB \rightarrow A + B^-$) might be employed to determine lower limits for associative-detachment cross sections ($A + B^- \rightarrow AB + e$), i.e., reverse of the attachment process. From the reciprocity theorem,³⁴ we have

$$\sigma_{(A+B^- \rightarrow AB+e)} = \left[\frac{\lambda_{A-B^-}}{\lambda_{e-AB}} \right]^2 \sigma_{(e+AB \rightarrow A+B^-)}, \quad (7)$$

where λ_{e-AB} is the deBroglie wavelength of the $e-AB$ system and λ_{A-B^-} is the deBroglie wavelength for the $A-B^-$ system. The associative-detachment cross section determined from Eq. (7) is only a lower limit since many more channels may be available (i.e., the neutral formed may be left in a state of vibrational and/or rotational excitation). As an example, a lower limit to the cross section for the reaction $\text{H}^- + \text{OH} \rightarrow \text{H}_2\text{O} + e$ is calculated to be $\sim 10^{-20}$ cm² for an H⁻ energy of ~ 2 eV.

³³ F. Fayard, in *Actions Chimiques et Biologiques des Radiations*, edited by H. Haissinsky (Masson, Paris, 1965), p. 63.

³⁴ J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1963), p. 337.

³² J. C. Y. Chen and J. L. Magee, *J. Chem. Phys.* **36**, 1407 (1962).

Notice from Eq. (7) that when the deBroglie wavelength of the $A-B^-$ system becomes very small, the associative-detachment cross section can become very large. Since the relative kinetic energy of the ions produced in CO at 9.7 eV and H₂ at 3.7 eV is approximately zero, large associative-detachment cross sections are to be expected for these molecules.

Equation (7) may be employed to place lower limits on many associative-detachment cross sections of interest in astrophysics. For example, the electron attachment data of Schulz³⁵ and Rapp *et al.*²⁹ predict a lower limit of $\sim 10^{-23}$ cm² for the reaction $H^- + H \rightleftharpoons H_2^-(^2\Pi_u) \rightleftharpoons H_2 + e$ for an H⁻ energy of ~ 7 eV.

³⁵ G. J. Schulz, *Phys. Rev.* **113**, 816 (1959).

Similarly, the reaction $H^- + H \rightleftharpoons H_2^-(^2\Pi_g) \rightleftharpoons H_2 + e$ could be quite large. Such a process has been suggested³⁶ as an important intermediate reaction in the formation of stars.

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³⁶ M. R. C. McDowell, *Observatory* **81**, 240 (1961).

Angular Correlation in the Helium Atom

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Schwartz has shown that if the wave function for the ground state of He is developed as a perturbation series in powers of $1/Z$ and if the first-order wave function is expanded in a series of Legendre polynomials in the angle θ between the position vectors of the electrons, the contribution of the P_l component to the second-order energy behaves as l^{-4} for large l . This same behavior is noted for a model atomic system.

THE relative importance of the various angular contributions to the second-order energy for the ground state of the helium atom where $1/Z$ provides a natural perturbation parameter has been discussed by Schwartz.^{1,2} He has reported that if the first-order wave function is expanded in a series of Legendre polynomials in the angle θ between the position vectors of the electrons; the contribution of the P_l component to the second-order energy behaves as l^{-4} for large l . Lakin³ has extended the result to the total energy. This same behavior is obtained for a model atomic system.

The model atomic system will be called the Hooke's law atom. It has been studied previously by Kestner and Sinanoglu⁴ and, using perturbation theory, by White and Byers Brown.⁵ In this model the electron-nucleus interaction is assumed to be harmonic while the electron-electron interaction remains Coulombic.

For both the actual helium atom and the Hooke's law model, the equation to be solved is

$$(H_0 - E_0)\psi_1 = -(V - E_1)\psi_0, \quad (1)$$

where $V = 1/r_{12}$. Writing

$$\psi_1 = F\psi_0 \quad (2)$$

in both cases and expanding F in a Legendre series in the angle θ between the two electrons

$$F = \sum_{l=0}^{\infty} f_l(r_1, r_2) P_l(\cos\theta) \quad (3)$$

reduces the problem to an infinite set of two-dimensional equations. In both cases the equation which determines f_l is

$$\left[\nabla_1^2 + \nabla_2^2 + \frac{\partial \ln \psi_0^2}{\partial r_1} \frac{\partial}{\partial r_1} + \frac{\partial \ln \psi_0^2}{\partial r_2} \frac{\partial}{\partial r_2} \right] f_l = 2 \left[\frac{r^{< l}}{r^{> l+1}} - E_1 \delta_{l0} \right], \quad (4)$$

$$\nabla^2 \rightarrow \frac{1}{r} \frac{\partial^2 r}{\partial r^2} - \frac{l(l+1)}{r^2}.$$

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¹ C. Schwartz, *Phys. Rev.* **126**, 1015 (1962).

² C. Schwartz, in *Methods in Computational Physics*, edited by B. Alder, S. Feinbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 262.

³ W. Lakin, *J. Chem. Phys.* **43**, 2954 (1965).

⁴ N. Kestner and O. Sinanoglu, *Phys. Rev.* **128**, 2687 (1962).

⁵ R. White and W. Byers Brown, University of Wisconsin Theoretical Chemistry Institute Report No. WIS-TCI-116, 1965 (unpublished).