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This final ARO report summarizes our results on electron collision with atmospheric gases and hydrocarbon molecules. Absolute cross sections for vibrational excitation, dissociative attachment and associative detachment were determined in 0-20 eV. The magnitudes and behavior of these processes were predominated by resonances. Recently we also developed two methods for studying inelastic cross sections at near thermal energies and negative ion formation from excited molecules. Perspectives of our past research and our outlook toward the future are presented.

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Final Technical Report

EXPERIMENTAL LABORATORY STUDIES ON ELECTRON COLLISION PROCESSES:

Atmospheric Gases, Hydrocarbons and Dyes

S. F. Wong

December, 1978

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DEPARTMENT OF ENGINEERING

AND APPLIED SCIENCE

YALE UNIVERSITY

TABLE OF CONTENTS

I. INTRODUCTION

In this final ARO report we describe our results under "Electron Collision Processes in Atmospheric Gases" during December 1972 - November 1975 and under "Inelastic Electron Collision in Hydrocarbons and Dyes" during December 1975 - November 1978. We also present our view on further work to take advantage of the new research developments obtained during the last period.

The electron collision group in the Department of Engineering and Applied Science was formed by George J. Schulz in 1966 and the research has since been supported by ARO. The results completed through November 1975 were summarized in the 1975 ARO proposal submitted by Schulz and in his three review articles on atoms (1973a), diatomic molecules (1973b), and triatomic molecules (1976). The main direction was to provide accurate measurements and an improved physical understanding of electron impact cross sections in atmospheric gases and others of technological interest.

The present principal investigator joined the group in June 1972 and has directed the electron impact program since George Schulz's death in January, 1976. The main goal in this December 1975 - November 1978 period was to extend resonant scattering experiments from diatomic to more complex molecules in view of potential infrared laser applications.

During the past three-year period, we have launched and established a new program on vibrational excitation of prototype hydrocarbon molecules in the 1-11 eV region. This was made possible by the recent improvements of high-resolution electron beam techniques. Our major results include the observation of high mode-selectivity in resonant vibrational excitation (Wong and Schulz, 1975), the isotope effects in rotational and vibrational cross sections (Chang and Wong, 1977), and a full-scale demonstration of the validity of resonance concept in prototype hydrocarbon molecules (Walker, Stamatovic, and Wong, 1978). In this period we also made notable advances in two experimental methods. For threshold inelastic studies we have established a new type of electron impact spectrometer (Tam and Wong, 1979) with usable impact energy from 20 eV down to 100 meV. For scattering involving excited molecules, our dissociative attachment apparatus has been improved to perform the first experiments on H^-/H_2 and D^-/D_2 with resolution of initial vibrational and selected rotational states (Allan and Wong, 1978).

In Section II we describe our experimental approaches and in Sections III and IV our results obtained in the December 1972 - November 1978 period. Section V gives the perspectives of our past and future research program. Section VI lists our publications supported by ARO and Section VII the references.

II. EXPERIMENTAL APPROACHES

We use several distinct methods to study scattering cross sections of interest. All of our work involves monoenergetic electrons, using either electrostatic energy analyzers or magnetic trochoidal energy analyzers. The scattering apparatus discussed below are made of molybdendum, which has desirable surface properties for low-energy electron scattering. We are equipped to obtain electron beams (either in a field-free space or in an axial magnetic field) with a half-width in·energy of 10-30 meV, or to analyze electrons with a resolution of 10-30 meV.

The vacuum systems we are using are of the ultra-high vacuum type, with metal gaskets, oil diffusion pumps with trapping and the apparatus chamber is of stainless steel construction.

The detection systems usually involve electron multipliers and pulse-counting techniques. Our main signal-averaging system includes a PDP-11 computer which can accept signals from three experiments on a time-shared basis and a PDP-8 computer dedicated to a single experiment.

A brief listing of our apparatus follows and full descriptions are available in the published articles. Among the developments in our experimental techniques during the last three years are i) the improvement of the resolution of the hemispherical electron spectrometer to 12 meV (half-width of energy-loss peaks) for high-resolution studies ii) the development of a new magnetic electron spectrometer for collision experiments at very low impact energies (0.1 - 20 eV), and iii) modification of the electron impact mass spectrometer for studies of negative ion formation with resolution of initial vibrational states.

A. Electrostatic Electron Impact Spectrometer

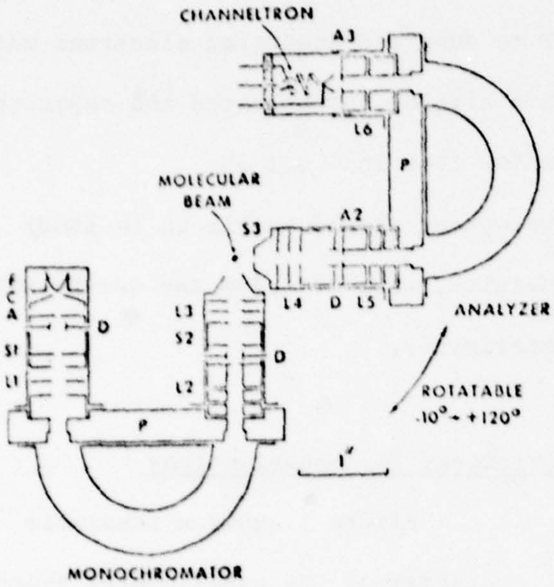

FIG. 1. Double Hemispherical Analyzer As Electron Impact Spectrometer

The electron impact apparatus shown in Fig. 1 consists of a rotatable hemispherical monochromator, a molecular beam which crosses the path of the incident electron beam, and a hemispherical analyzer to examine the scattered electrons.

Energy dependences of differential cross sections can be measured, as well as energy-loss and constant-residual energy spectra. Total cross sections are obtained by integrating the angular dependence of the differential cross sections. This spectrometer has been used extensively for vibrational and rotational cross section studies (e.g. Boness and Schulz, 1974; Wong and Dubé, 1978).

B. Magnetic Electron Impact Spectrometer

A new type of electron impact spectrometer using an axial magnetic field for electron collimation was developed (Tam and Wong, 1979). The apparatus is shown in Fig. 2. It utilizes two trochoidal monochromators (Stamatovic and

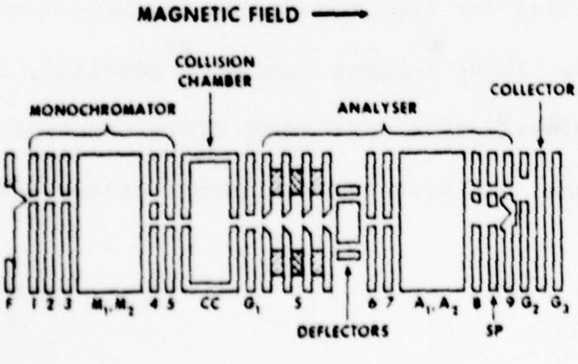

FIG. 2. Double Trochoidal Analyzer As Electron Impact Spectrometer.

Schulz, 1970) as electron monochromator and analyzer. An electron filter S is placed behind the collision chamber to suppress scattered electrons which have large transverse energies. We have already demonstrated the capacity of this spectrometer for collision studies from 20 - 0.1 eV.

We anticipate that further development should enable us to study inelastic processes down to thermal energies, thus bridging the energy gap between conventional beam and swarm experiments.

C. Electron Impact Mass Spectrometer For Negative Ions

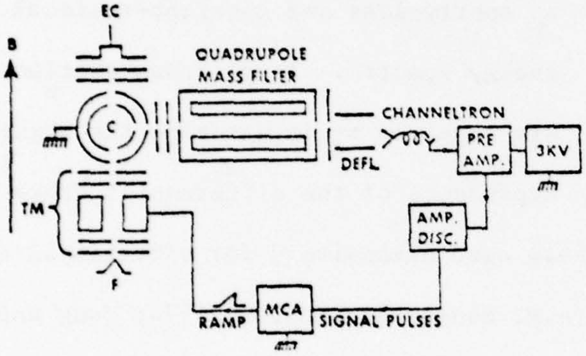

FIG. 3. Electron Impact Quadrupole Mass Spectrometer

Figure 3 shows a schematic diagram of the experimental system. The apparatus consists of a trochoidal monochromator for monoenergetic electrons, an iridium collision chamber in which the electron beam is intercepted by gas molecules, and a quadrupole mass filter to analyze the positive or negative ions formed in the collision chamber. This system has been used for dissociative attachment studies of small molecules (e.g. Ziesel, Nenner and Schulz, 1975). The ion optics and collision chamber has been recently modified for high resolution studies of molecules at high temperatures to 1500°K. These changes have made possible, for the first time, the study of dissociative attachment cross sections with resolution of initial vibrational and selected rotational states (Allan and Wong, 1978).

D. Ion Impact Apparatus for Associative Detachment

This apparatus was developed during the 1972 - 1975 period and a schematic diagram is shown in Fig. 4. A beam of negative ions, formed at low kinetic energy by electron impact in the ion source is made monoenergetic and is incident on the collision chamber, in which the detachment process takes place. A magnetic field (B) is applied in the direction indicated on Fig. 4. Electrons (marked e) which are produced in the collision chamber traverse a retarding-potential region and are counted following multiplication by the channeltron electron multiplier. This apparatus has been used for measurements of electron-detachment cross sections in collisions involving O^- and S^- with a variety of molecules of atmospheric interest (Mauer and Schulz, 1973; Comer and Schulz, 1974). The incident ion energy is in the range 0.5 to 20 eV. This intermediate energy region contains the thresholds for many important processes and is not covered satisfactorily by any other technique.

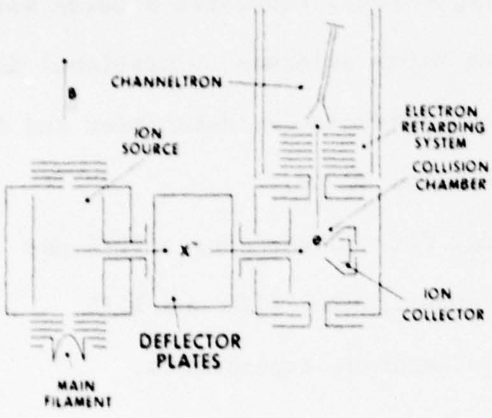

FIG. 4. Magnetic Ion Impact Apparatus

III. RESULTS DURING THE 1972-1975 YEARS

In this section we give an overview of the results we have obtained in the 1972-1975 period. Most of them have been described in the 1975 ARO proposal submitted by Schulz. Much more detail can be found in the papers listed in Section VI.

In this period we concentrated our efforts toward atmospheric gases such as O_2, N_2, CO, N_2O, ... Among the physical processes studied was the role of compound states in scattering cross sections (vibrational and total) and in ion formation cross sections (associative detachment and dissociative attachment) at impact energies below 20 eV.

We describe below these results under four subsections. IIIA and IIIB cover vibrational and transmission experiments, IIIC and IIID associative detachment and dissociative attachment experiments.

A. Resonances in Vibrational Cross Sections

We have studied several vibrational cross sections during this contract period. Among them was a study of O_2 and N_2O. The results of which reveal the important role of second shape resonances (broad compound states) on vibrational excitation. We also studied the vibrational excitation of some hydrogen halides and observed threshold spikes in vibrational excitation cross sections. A transmission method was used to map the resonances in simple hydrocarbons and laid the ground work for the hydrocarbon program in the 1975-1978 period.

A-1. Vibrational Excitation in O_2 and N_2O

Whereas the vibrational excitation in the range 0-2 eV had been previously studied by Linder and Schmidt, we studied vibrational excitation at higher energies, in the range 4 - 14 eV. In this energy range, we find bell-shaped curves for v = 1 - 4, with no structure apparent. The results are shown in Fig. 5. In the same energy range, we find an enhancement of the low-lying electronic cross sections ($a^1\Delta_g$ and $b^1\Sigma_g^+$) as well, which is shown in Fig. 6. We interpret the vibrational cross section shown in Fig. 5 as evidence for a higher shape resonance, probably $^4\Sigma_u^-$.

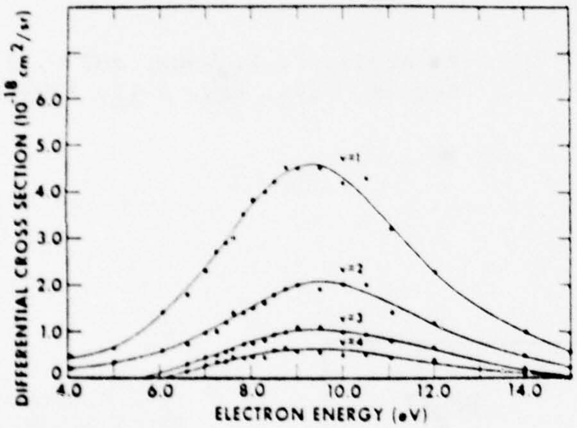

FIG. 5. Energy dependence of the differential vibrational cross sections for $v = 1 - 4$ of $X^3\Sigma_g^-$. The experimental errors in the cross sections are about 30%.

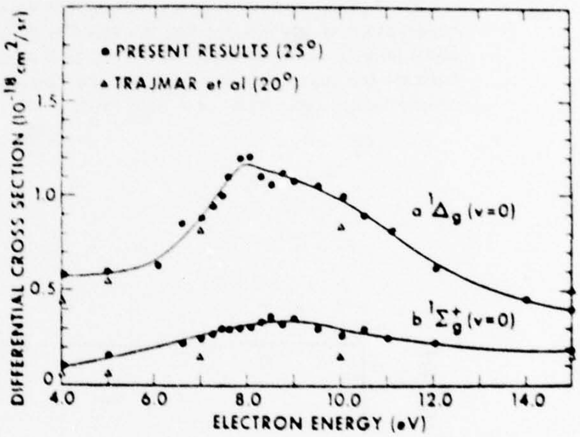

FIG. 6. Energy dependence of the differential electronic cross sections for the states $a\,^1\Delta_g$ ($v = 0$) and $b\,^1\Sigma_g^+$ ($v = 0$). The experimental errors in the cross sections are about 35%.

S. F. Wong, M. J. W. Boness and G. J. Schulz, Phys. Rev. Letters 31, 969 (1973).

In fact, the results for vibrational excitation in O_2 described in connection with Fig. 5 are not dissimilar to the vibrational excitation in N_2O, in the energy range 1.6 - 3 eV, which we studied as well. Here, we are dealing with the $^2\Sigma^+$ resonance in N_2O^-, which is the second shape resonance in the N_2O system. Fig. 7 shows the dominant vibrational modes excited at incident electron energies on and off the center (2.3 eV) of

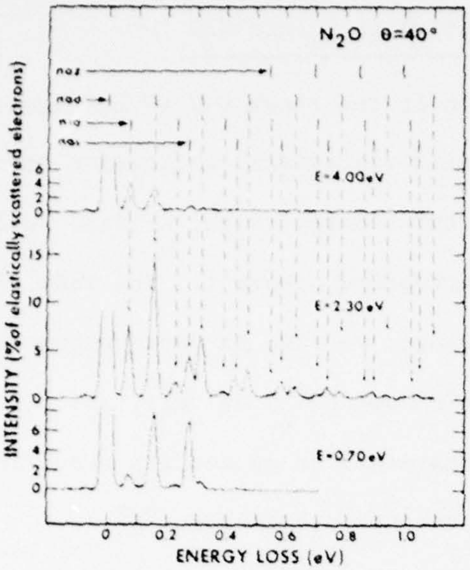

FIG. 7. Energy-loss spectra obtained at an angle of observation of 40° and incident energies of 0.70, 2.30, and 4.00 eV, respectively. On the top of the figure we indicate the calculated positions for the vibrational progressions $n00$, $n10$, $(n-3)02$, $n01$.

this resonance. Among all normal modes, only the totally symmetric mode 100 develops into three strong series: n00, n10, and n01. Fig. 8 shows the energy dependencies for two strong modes, 200 and 110. These cross sections shown in Fig. 8 are of the same order as those in O_2 of Fig. 5.

R. Azria, S. F. Wong, and G. J. Schulz, Phys. Rev. A <u>11</u>, 1309 (1975)

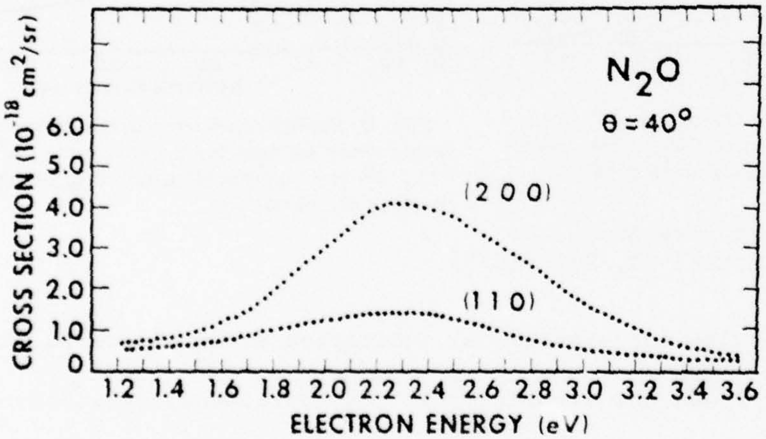

FIG. 8. Energy dependence of the differential cross sections for the 200 and 110 modes. The absence of any structure in these curves points to the possibility that a short-lived resonance is involved in populating the vibrational states in this energy range. The estimated error for the cross section scale is about 35%.

R. Azria, S. F. Wong, and G. J. Schulz, Phys. Rev. A <u>11</u>, 1309 (1975).

A-2. Vibrational Excitation in Hydrogen Halides

In the hydrogen halides, e.g. HCℓ or DCℓ, the vibrational excitation exhibits a very different character. This is probably the result of the large dipole moment which is characteristic of these hydrogen halides. The theoretical basis for this class of molecules is not as well established as one may wish. Using the trapped-electron method, we obtained some preliminary information on the vibrational excitation in HCℓ. The cross section for v = 1 rises steeply near threshold and it attains a value of $2 \times 10^{-16} - 10^{-15}$ cm^2 about 60 meV above threshold. The cross section for v = 2 is a factor of ten smaller. The transmission spectrum, as well as negative ion formation in HCℓ, DCℓ, HBr and DBr were studied as well (Ziesel, Nenner and Schulz, 1975).

Linder's group at Kaiserslautern did a systematic study of the vibrational excitation on similar molecules (Seng and Linder, 1976; Rohr and Linder, 1976) using a double-electrostatic analyzer. They observed enormously large threshold spikes in vibrational cross sections consistent with our earlier results. The more recent developments in polar molecules regarding experiments have been reviewed by Linder (1979). We shall discuss this work further in Section V.

B. Transmission Spectroscopy and Resonances in Simple Hydrocarbons

The simplest method we have for a study of resonances whose widths are relatively sharp (0.05 - 1 eV) is the "transmission method". The apparatus for these kind of studies is shown schematically in Fig. 9. Structure in the transmitted current is mostly (but not entirely) due to resonances. The derivative of the transmitted current, at low energies in benzene is shown in Fig. 10. We interpret the structures as an indication for a resonance (near 1.15 eV), with vibrational structure in the resonant state. We expect that vibrational excitation proceeds via this resonance, but this effect has not yet been studied. Numerous molecules have been studied by this method, giving us a preliminary indication what to expect when more detailed studies of vibrational excitation are undertaken.

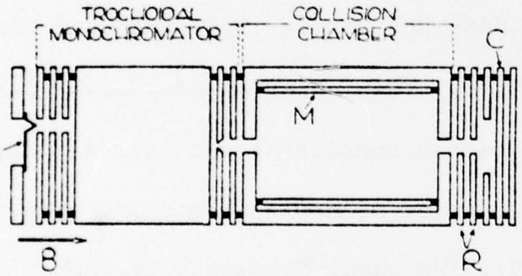

FIG. 9. Schematic diagram of the electron transmission spectrometer. Electrons emitted from the filament F are aligned by a magnetic field B and energy selected by a trochoidal monochromator. The monochromatic electron beam then passes through the collision chamber where a small modulating signal (5–50 meV, 730 Hz) is applied to cylinder M. The transmitted current is detected synchronously at the collector C. The retarding electrodes R provide a potential barrier for scattered electrons.

L. Sanche and G. J. Schulz,
J. Chem. Phys. 58, 479 (1973).

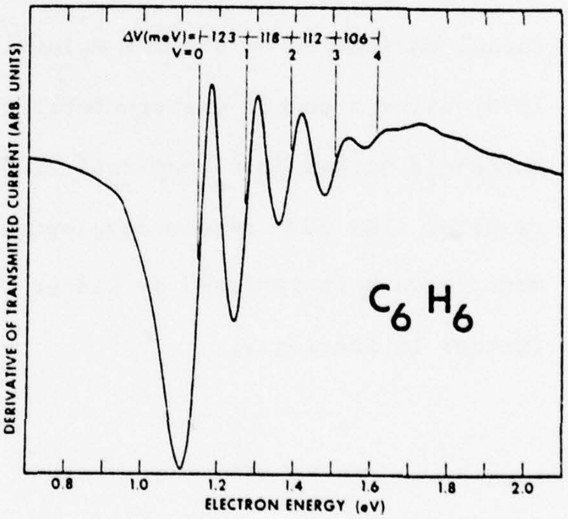

FIG. 10 Derivative of the transmitted current vs electron energy in the 1–2 eV region in benzene, plotted on an extended energy scale. Vertical lines indicate the center of each resonance. The vibrational spacings for the $^2E_{2u}$ state of $C_6H_6^-$ are shown between the vertical lines.

C. Associative Detachment

Negative ions can lose their extra electron in a number of ways in a collision with another atom or a molecule. The most effective way for the electron loss is the process called associative detachment. The reaction can be written schematically as follows:

(1) $$X^- + Y \rightarrow XY + e \quad .$$

Here, X^- is the negative ion (we have chosen to study O^- and S^-) and Y is either an atom or a molecule (we have studied CO, H_2, O_2, N_2, CO_2, NO, C_2H_2, C_2H_4 and CH_4). The above process is of interest both from a technological and a fundamental viewpoint. In discharges containing for example O_2 or CO_2, copious negative ions are formed. These negative ions influence the stability of discharges and the diffusion characteristics. Associative detachment by virtue of its large cross section is an important mechanism for the destruction of the negative ions and for production of free electrons. From a collisional viewpoint, the interest centers on the fact that an intermediate state ("compound state" or "resonance") is involved in the reaction and actually reaction (1) proceeds as follows

(2) $$X^- + Y \rightarrow XY^- \rightarrow XY(v) + e$$

where XY^- is the intermediate state with a lifetime of the order of $10^{-15} - 10^{-14}$ sec. The final product, XY can be vibrationally excited.

We have measured the value and the energy dependence of the associative detachment cross section. We have also started on the measurement of the kinetic energy of electrons coming off in this reaction. The experimental apparatus used for this line of work has been described in Section II D and numerous results obtained are available in the publications listed in Section VI.

As a sample of the results obtained, we show in Fig. 11 the detachment cross section vs. kinetic energy in the center-of-mass system for $O^- + N_2$. These results are important for an analysis of swarm experiments in air, but the curve of Fig. 11, which extends down to 320 meV became somewhat controversial: Ferguson's group (1974) at NBS, Boulder, found no measurable detachment in a drift experiment in which the average energy of the ions is in the range of 300 meV. The reason for this discrepancy is not understood at present.

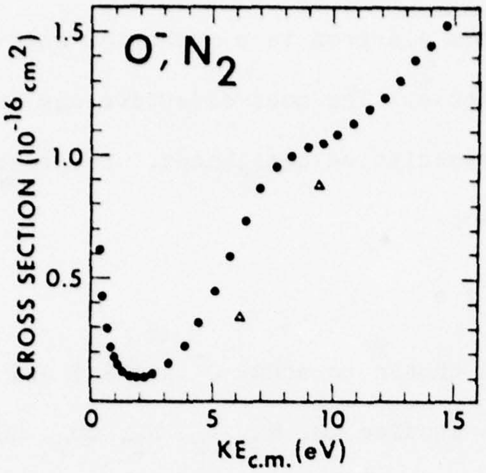

FIG. 11. Electron detachment for $O^- + N_2$. The data are ●, present work; △, Roche and Goodyear.

J. Comer and G. J. Schulz,
Phys. Rev. A 10, 2100 (1974).

An additional important observation has been made: When we measure the energy of the electrons which are liberated in the associative detachment reaction we find that the kinetic energy is generally low, thus indicating the molecule being formed as a result of the associative detachment reaction is vibrationally excited. This observation can be understood in terms of the crossing of potential energy curves of the XY^- system and the $X^- + Y$ system, as is shown schematically in Fig. 12.

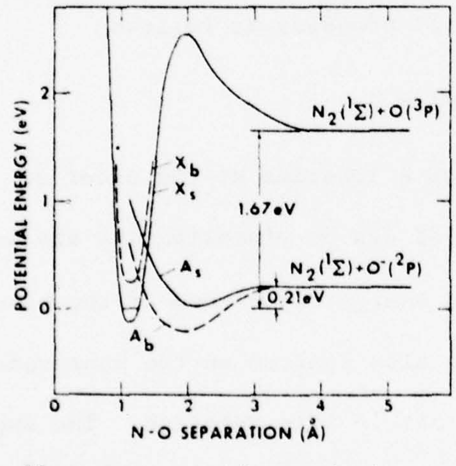

FIG. 12. Schematic potential curves for the states $N_2O(X)$ and $N_2O^-(A)$ in which subscripts *s* and *b* refer to the straight and bent species, respectively. These curves are similar to the ones given by Chantry.

J. Comer and G. J. Schulz,
Phys. Rev. A 10, 2100 (1974).

D. Dissociative Attachment

Our studies of negative ion formation were mostly done during the early part of the 1972-1975 period. We are equipped for the measurement of the total negative ion cross section and for the measurement of individual negative ions, using mass spectrometry. In either system we are able to vary the temperature of the target gas by heating the collision chamber, which consists of a thin iridium cylinder, through which a current of up to 100 Amp can be passed.

D-1. Attachment to Polyatomic Molecules

Rather interesting results were found when the total attachment cross section (i.e. negative ion formation) was measured near zero electron energy and when the temperature of the target gas was varied. Fig. 13 shows the result. Of course, the change in temperature alters the vibrational and rotational population of the target gas.

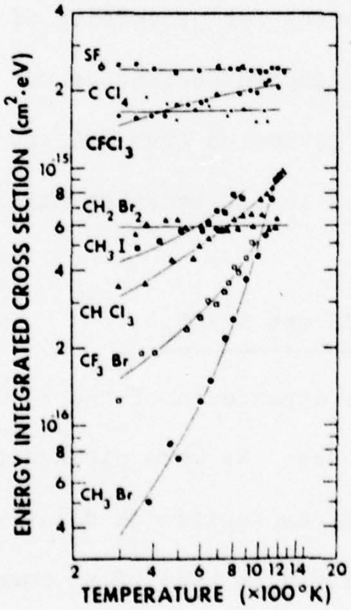

FIG. 13 Temperature dependence of the energy integrated cross sections for total negative ion production in SF_6 and a group of halogenated methanes.

D. Spence and G. J. Schulz, J. Chem. Phys. 58, 1800 (1973).

It is immediately obvious from Fig. 13 that the integrated attachment cross section for the various molecules shows a wide range of values at room temperature, the values extending over a range of two orders of magnitude. At 1000°K, the range of values is only a factor of 4. Further, one notices that the smaller the attachment cross section of a molecule at room temperature, the larger is the temperature dependence. The molecule CH_2Br_2 is the exception. Although the attachment cross sections appear to be approaching a common value as the gas temperature increases, this temperature is not within the range of the present apparatus. Sulfur hexafluoride, SF_6, does not exhibit a temperature variation, the cross section remaining constant up to 1200°K. This indicates that the cross section for SF_6^{-*} formation does not depend on the initial vibrational state of SF_6. It should be noted that the species of negative ions formed near zero energy (SF_6^-, SF_5^-, F^-) depends strongly on temperature, but this is not inconsistent with the present observations if one postulates that the decay channels of the compound state depend on temperature.

D-2. S^- From OCS and CS_2; O_2^- and C^- From CO_2; $C\ell^-$ From HCℓ and DCℓ

Various dissociative attachment processes, which became of interest for various reasons, have been examined. In the case of S^-/OCS and S^-/CS_2, we were interested in finding a source for production of S^- ions; in the case of O_2^- and C^- from CO_2, we attempted to improve our understanding of the CO_2 molecule; in the case $C\ell^-$ formation from HCℓ and DCℓ we were searching for regions of resonances in the hydrogen halides.

D-3. S^-/OCS and S^-/CS_2

Figs. 14 and 15 show the energy dependence of the S^- cross sections and Table I gives the absolute magnitudes. We were pleased to learn that the absolute magnitude of the S^-/OCS cross section is relatively large and we have employed this effect for producing a beam of S^- ions.

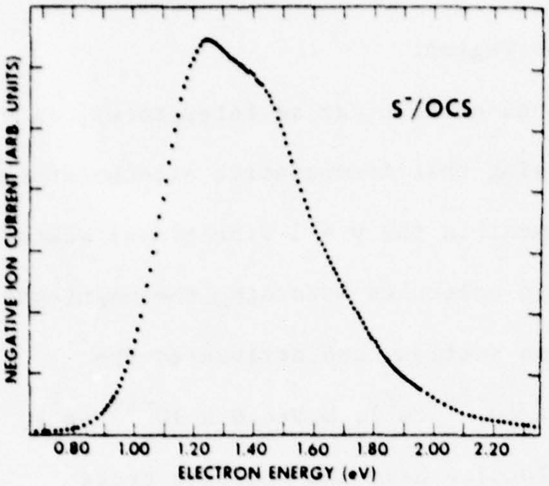

FIG. 14. Formation of S^- in OCS. The electron energy scale corresponds to the most probable electron energy.

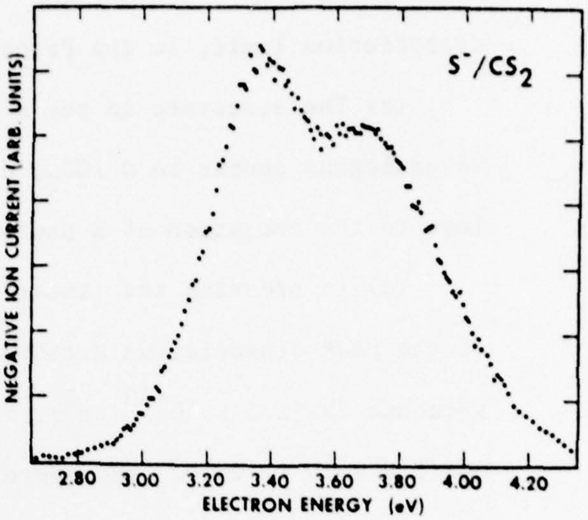

FIG. 15. Formation of S^- in CS_2. The electron energy scale corresponds to the most probable electron energy.

TABLE I. Cross sections for negative ion formation in OCS, CS_2, and CO_2 at 300 °K.

Ion	Energy at peak (eV)	Peak cross section (cm²)	Q, at 30 eV (cm²)
S^-/OCS	1.25	2.9×10^{-17}	4.2×10^{-16}
S^-/CS_2	3.35	3.7×10^{-19}	7.5×10^{-16}
O^-/CO_2	1.4	1.5×10^{-19}	1.7×10^{-16}

J. P. Ziesel, G. J. Schulz and J. Milhaud, J. Chem. Phys. <u>62</u>, 1936 (1975).

We also compared the properties of dissociative attachment of COS, CS_2 and CO_2 to arrive at some generalization of this process in triatomic molecules:

(a) The onsets for O^-/CO_2 and S^-/OCS processes are close to the dissociation limit, unlike the onset for S^- from CS_2 which occurs about 0.5 eV higher. These observations suggest that the potential energy surface of OCS^- must be attractive in a part of the Franck-Condon region, similar to the CO_2^- surface. The delayed onset and the steep threshold region of the S^-/CS_2 cross section suggest that a hump is present in the CS_2^- potential energy surface.

(b) The thresholds for O^-/CO_2, S^-/OCS, and S^-/CS_2 are not "vertical," as would be expected from the existence of the compound state below the dissociation limit, in the Franck-Condon region.

(c) The structure in the S^-/OCS cross section can be interpreted, in an analogous manner to O^-/CO_2, by supposing that dissociative attachment can lead to the formation of a neutral fragment in the $v = 1$ vibrational state.

(d) In ordering the linear triatomic molecules according the magnitude of the peak dissociative attachment cross section, one arrives at the sequence $CO_2(1.5 \times 10^{-19}\ cm^2)$, $CS_2(3.7 \times 10^{-19}\ cm^2)$, $N_2O(8.6 \times 10^{-18}\ cm^2)$, $OCS(2.9 \times 10^{-17}\ cm^2)$. The symmetric molecules have the smallest cross sections.

D-4. O_2^- and C^- from CO_2

We observed the formation of O_2^- ions and C^- ions by dissociative attachment to CO_2. The cross sections for these processes are, however small ($10^{-24}\ cm^2$ and 2×10^{-21} for O_2^- and C^- respectively). Nevertheless, these observations added to the understanding of the potential energy curves of CO_2.

D-5. $C\ell^-$ and Br^- from Hydrogen Halides

The formation of $C\ell^-$ and Br^- from $HC\ell$ ($DC\ell$) and HBr (DBr) shows a steep onset near threshold and structure at higher energies. This structure occurs at the energies of the vibrational levels of the $X^1\Sigma^+$ ground state of the hydrogen halide, as shown in Fig. 16. Similar structure is observed in the other hydrogen halides, but a detailed understanding for the processes causing this structure is still lacking. We can speculate that it is caused by the competition between dissociative attachment and vibrational excitation, a mechanism that has been proposed by Fiquet-Fayard.

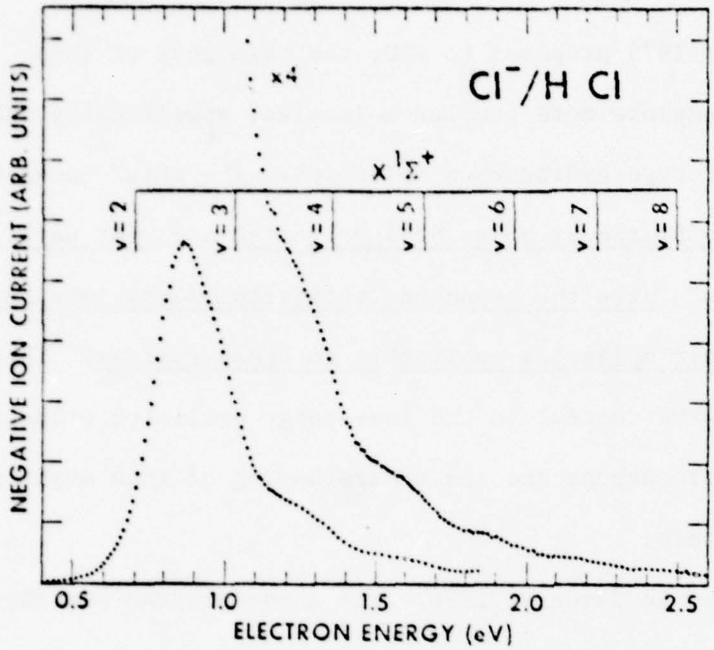

FIG. 16. Cross section for $C\ell^-$ formation from $HC\ell$ by dissociative electron attachment. The energies of the vibrational levels of the $HC\ell(^1\Sigma^+)$ ground electronic state are indicated by vertical bars.

J. P. Ziesel, I. Nenner and G. J. Schulz, J. Chem. Phys. <u>63</u>, 1943 (1975).

IV. RESULTS DURING THE 1975-1978 YEARS

As given in Schulz's 1975 proposal to ARO, the main goal of this 1975-1978 period was to explore more complex molecules, specifically vibrational excitation of prototype hydrocarbon molecules. The chief questions at that time were *which vibrational modes became excited* and *what were their energy dependencies*? *Were the resonance excitation mechanisms learned from diatomic and triatomic molecules applicable to these systems*? These questions, we believed, were central to the low-energy collision processes between electrons and hydrocarbons and the understanding of them might shed light on new infrared lasers.

George J. Schulz died in January, 1976. The above program was then directed by the present principal investigator and was established by November, 1978.

Our findings in the hydrocarbon program are characterized by three papers. In benzene (Wong and Schulz, 1975) we observed high selectivity in normal modes by electron impact and formulated selection rules for resonant vibrational excitation. In hydrogen (Chang and Wong, 1976) we observed isotope effects in vibrational cross sections and made predictions for hydrocarbons. In ethylene (Walker, Stamatovic, and Wong, 1978) we used the energy-loss spectra, angular and energy dependence of absolute vibrational cross sections to show the important role of resonances on vibrational excitation and confirmed the ideas advanced in the two earlier papers.

In addition to establishing the hydrocarbon program, we have also made major advances in two new lines of experimental techniques in the 1975-1978 period. The first is a new kind of electron spectrometer which has the potential of inelastic collision studies from 20 eV down to 0.1 eV

(Tam and Wong, 1979). We expect that further refinement will enable us to reach thermal energy region, thus filling the energy gap between conventional beam and swarm experiments. The second is via improving our electron impact mass spectrometer, we have made possible the first study of dissociative attachment from hot molecules with resolution of initial vibrational and selected rotational states (Allan and Wong, 1978).

We summarize below the results we have obtained under the present grant during the period 1975-1978. Details can be found in the papers listed in Section VI .

A. Vibrational Excitation of Hydrocarbon Molecules

Three different prototype molecules, namely C_6H_6, C_2H_4, and CH_4 have been selected for studies. As will be seen below, their varied geometries and molecular structures yield distinctly different information in regard to resonant excitation. The major findings include the observation of i) high selectivity of normal modes in resonant excitation, ii) new broad resonances, and iii) the generally large magnitude ($\sim Å^2$) of vibrational cross sections.

A-1. C_6H_6 and C_6D_6

We chose benzene, a highly symmetric molecule belonging to the D_{6h} point group, as a starting point to develop an understanding for vibrational excitation in hydrocarbons. Previous transmission experiments performed in this laboratory located two shape resonances at 1.2 eV ($^2E_{2u}$ symmetry) and at 4.8 eV ($^2B_{2g}$ symmetry). Our initial crossed-beam electron scattering experiments revealed that the resonant vibrational excitation is highly selective. Despite the fact that benzene possesses a large number of normal modes (10 degenerate ones plus 10 doubly degenerate ones), only three normal modes (ν_2, ν_{16}, and ν_{20}) are strongly excited via the 1.2 eV resonance and two normal modes (ν_1 and ν_7) are excited via the 4.8 eV resonance. We found that this selective vibrational excitation can be understood in terms of <u>selection rules</u> based on symmetry considerations. Fig.17 and Table II highlight the findings in the 1.2 eV resonance.

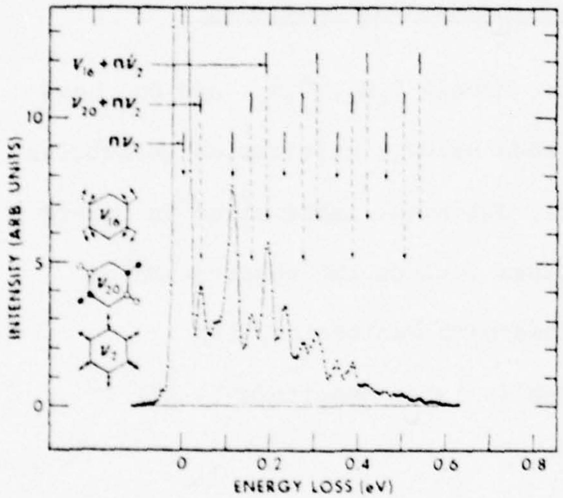

FIG. 17. Energy-loss spectrum in C_6D_6 at an incident energy of 1.18 eV (the ground vibrational level of the $^2E_{2u}$ resonance) and an angle of observation of 70°. Only the modes ν_2, ν_{16}, and ν_{20} (Herzberg's notation) become appreciably excited. The geometry of these modes is indicated. Only one each of the doubly degenerate modes for ν_{16} and ν_{20} are shown.

TABLE II. Vibrational modes excited via the 4.8-eV resonance in benzene. Selection rule: g_π - s_σ - nonrigid constraint. ν_7 and ν_8 are out-of-plane modes.

	Symmetry			
	a_{1g}		b_{2g}	
g_π wave (b_{2g})	ν_1	ν_2		
s_σ wave (a_{1g})			ν_7	ν_8
Nonrigid C-H	×		×	
Strongly obs.	×		×	

S. F. Wong and G. J. Schulz,
Phys. Rev. Letters <u>35</u>, 1429
(1975).

Since the publication of the above Phys. Rev. Letter, the energy and angular dependences of the vibrational cross sections via the $^2E_{2u}$ shape resonance (1-3 eV) have also been studied. The energy dependence of the vibrational cross sections for the normal modes ν_2, ν_{16}, and ν_{20} all exhibit orders of magnitude enhancement and fine structures in the resonance region, reminescent to that of the 2.3 eV resonance in N_2. The energy and angular dependences for excitation to these three normal modes are distinctly different. Using the angular correlation theory similar to that developed by Read (1968), we have been able to account for the general shapes of the differential cross sections for ν_2, ν_{16}, and ν_{20} by invoking the differences in the symmetries of the normal modes (a_{1g}, e_{2g}, and e_{2u} respectively) and other assumptions based on simple physical arguments.

A-2. C_2H_4 and C_2D_4

We consider the ideas of selection rules and the role of symmetry in the angular dependence derived from our benzene studies merit further tests in other prototype hydrocarbons. A detailed study of C_2H_4 and its fully deuterated counterpart, C_2D_4, has been carried out in the energy range 1-11 eV.

Unlike benzene, etheylene belongs to the D_{2h} group and has a much reduced symmetry. Previous transmission experiments have located only one broad shape resonance centered at 2.0 eV with an expected symmetry of $^2B_{2g}$.

We have studied the differential and total cross sections for electron energies between 1 and 10 eV. Fig.18 shows the energy dependence of the differential cross sections for various energy losses. The vibrational excitation is dominated by two resonance regions centered near 2 and 8 eV respectively. Among the twelve normal modes of ethylene, only two symmetries of vibrational modes (a_g: ν_1,ν_2, and ν_3; b_{3u}: ν_7) are strongly excited via resonances, which is consistent with the expectation of selection rules developed in the benzene work.

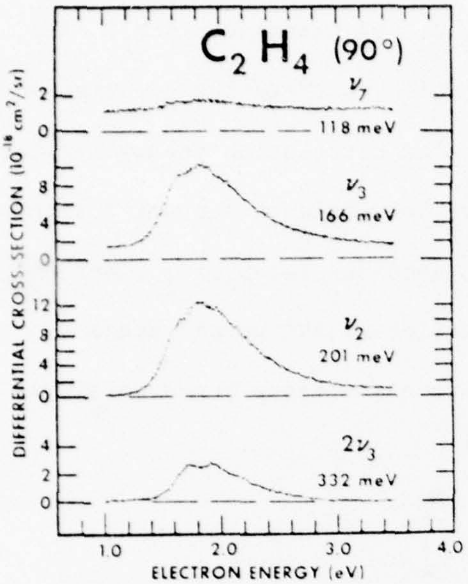

FIG. 18. Energy dependence of absolute differential cross sections for four different energy losses in the 1.8 eV resonance region.

I. C. Walker, A. Stamatovic, and S. F. Wong, J. Chem. Phys. 69, 5532 (1978).

The angular dependences of the absolute differential cross sections for the fundamental modes are shown in Figs. 19 and 20.

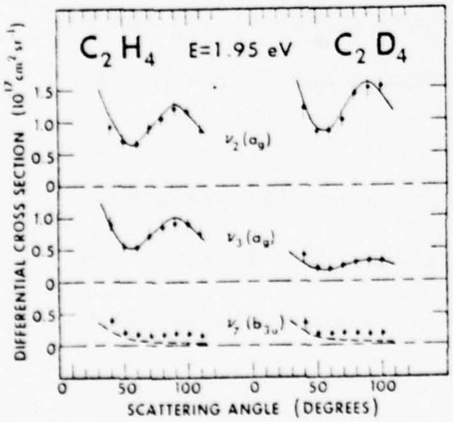

FIG. 19. Angular distributions of three strongly excite in C_2H_4 and C_2D_4 at an incident energy of 1.95 eV.

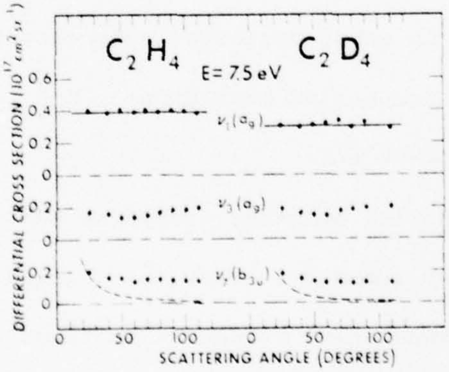

FIG. 20. Angular distributions of three strongly excited modes in C_2H_4 and C_2D_4 at 7.5 eV.

I. C. Walker, A. Stamatovic, and S. F. Wong, J. Chem. Phys. 69, 5532 (1978).

In the 2 eV resonance region, the fundamental modes ν_2 and ν_3 are most strongly excited and their angular distribution is consistent with d partial wave scattering. All these observations in the 2 eV region can thus be understood in terms of a $^2B_{2g}$ shape resonance. In the 8 eV region, the strong excitation of ν_1 and ν_2 modes and the near isotropic behavior in their angular dependences lead us to interpret in terms of a second shape resonance with $^2\Sigma_g$ symmetry, in which the incident electron is trapped in the lowest Rydberg orbital ($4a_g$). Fig.21 shows the strongly observed normal modes and the associated resonances in the 1 - 11 eV range.

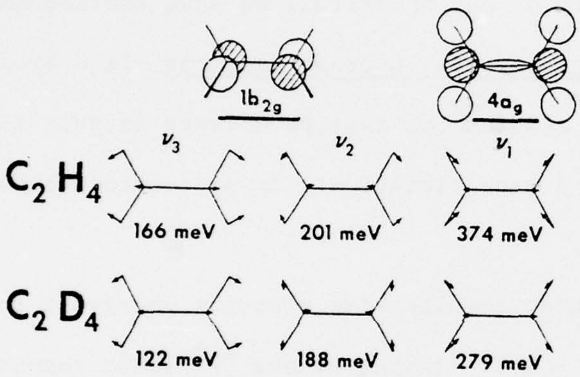

FIG.21. Schematic diagram illustrating the mechanism for selective resonant excitation among the normal modes of a_g symmetry in ethylene. The upper diagram shows the schematic charge distributions of the $1b_{2g}$ and $4a_g$ resonant orbitals

I. C. Walker, A. Stamatovic, and S. F. Wong, J. Chem. Phys. 69, 5532 (1978).

In summary, vibrational excitation of ethylene by electron impact at low energies, as in many diatomic and triatomic molecules, is dominated by shape resonances. We find that the energy-loss spectra and energy and angular dependences of vibrational cross sections in ethylene can be understood using (i) the resonant orbital and partial wave concepts developed for simpler systems, together with (ii) the recently postulated selection rules. Further, resonant vibrational excitation in prototype hydrocarbons, benzene and ethylene, seems remarkably sensitive to the symmetries of the orbitals and nuclear motion of the molecules. For example, in the second resonance region of C_2H_4, the incident electron excites predominantly a single vibrational mode ν_1 over a broad energy range ($\sim$ 4 eV). This efficient transfer of electron kinetic energy to a specific vibrational mode might yield new possibilities to novel infrared lasers.

A-3. Isotope Effects in Vibrational Excitation Cross Sections

In view of the complexity of hydrocarbon molecules, we are particularly interested in obtaining general rules and insights on the excitation process as well as the magnitudes of cross sections. With further improvement in resolution and sensitivity of our apparatus, we have carried out a fundamental study of the isotope effects in cross sections via a broad resonance. Specifically we have studied the isotope effects in pure rotational, rotational-vibrational and pure vibrational cross sections between H_2 and D_2.

Figure 22 shows the experimental results with electron energy at the center of the $^2\Sigma_u^+$ shape resonance. The half-width of all energy-loss peaks is 11.5 meV. The separation of the main peaks ($\Delta j = 0$) in D_2 is smaller than that in H_2 in accordance with the well-known vibrational spacing dependence on $\mu^{-1/2}$. Profiles of the rotational transition peaks are dictated primarily by the rotational-energy-

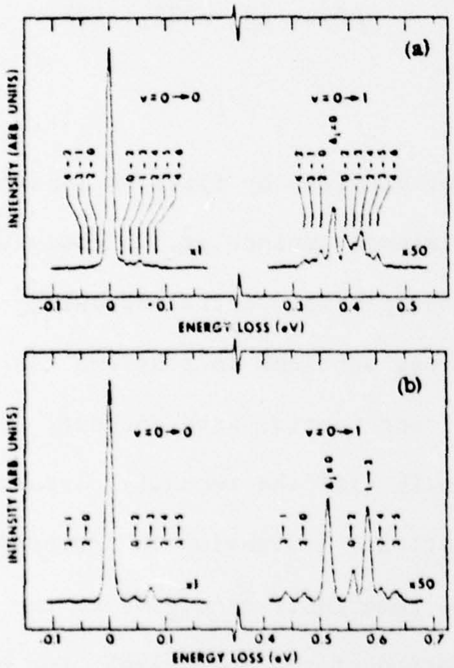

FIG. 22(a) Intensity of electron scattering in D_2 plotted against energy loss measured at 90° and at a fixed incident energy of 4 eV. Vibrational and rotational transitions are identified. (b) Same in H_2.

E. S. Chang and S. F. Wong, Phys. Rev. Letters <u>38</u>, 1327 (1977).

spacing dependence on μ^{-1} and by the rotational-level populations. Table III summarizes the experimental findings and interpretation based on the frame transformation theory (E. S. Chang and U. Fano, 1972).

TABLE III Ratio of D_2 to H_2 cross section at 90° and 4 eV.

Cross sections	Theory[a]	Experiment[b]				
		$\Delta j = 0$	$j = 0$	$j = 1$	$j = 2$	$j = 3$
Rotational ($v = 0 \to 0, j \to j + 2$)	1.00		0.96	1.10	0.80	1.15
Vibration-rotational ($v = 0 \to 1, j \to j + 2$)	0.71		0.72	0.79	0.72	0.78
Elastic ($v = 0 \to 0, \Delta j = 0$)	1.00	1.05				
Pure vibrational ($v = 0 \to 1, \Delta j = 0$)	0.56	0.55				

[a] Estimated accuracy is 1%.

[b] Except for the elastic result, all others are measured as ratios to the elastic cross sections. The estimated errors are 5% for the elastic, and about 10% for the other measurements.

E. S. Chang and S. F. Wong, Phys. Rev. Letters 38, 1327 (1977).

It follows from the scattering theory that isotope substitution produces two distinct effects in differential cross sections. One is due to the reduced mass μ. It causes cross sections to be multipled by a factor $\mu^{-v/2}$ where v is the final vibrational level. The other is due to the differences in rotational state populations which affect only the elastic and the pure vibrational cross sections. This view explains the experimental observations and is also supported by the impulse-limit and adiabatic-nuclei theories (private communications with A. Herzenberg and A. Temkin respectively).

We found in the following ethylene experiment (Walker, Stamatovic, and Wong, 1978) that the isotope effects observed in H_2 and D_2 were equally applicable to C_2H_4 and C_2D_4 when the vibrational modes mimic that in a diatomic molecule. We thus felt that a future rigorous theory on the isotope effects in polyatomic molecules should provide much insight to the energy transfer processes in hydrocarbons.

B. Magnetic Electron Impact Spectrometer

Electron impact studies of inelastic cross sections with electrostatic energy analyzers are usually limited to a lowest energy of about 0.5 eV due to difficulties associated with electron optics. The vibrational cross sections for most molecules are thus rarely studied in the threshold region and the excited mechanisms are not well understood. At low impact energies, the long wavelength of the incident electron makes possible a potentially very large cross section. A good example is the recent work of Linder's group on hydrogen halides (F. Linder, 1977).

A new type of electron impact spectrometer using an axial magnetic field for electron collimation has been developed in our laboratory. The design and operation principle has been discussed in Sec. II. The feasibility of this spectrometer for collision studies at low impact energies (0.1 - 2.0 eV) is demonstrated with various experimental measurements

One significant feature of the magnetic energy analyzer is the predictability of its transmission function down to zero energy. Fig. 23 shows the experimental energy-loss spectrum of threshold ionization in He and the correction for the transmission of the analyzer in the 0-1.5 eV region.

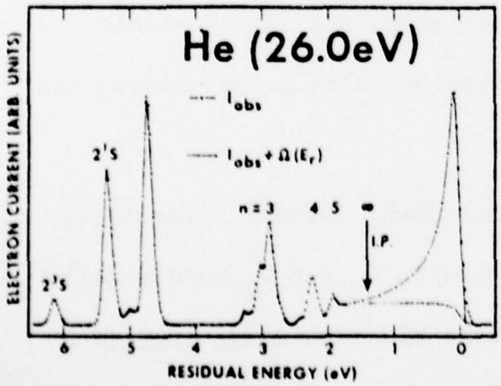

FIG. 23. Energy-loss spectrum of He at 26.0 eV. The steplike curve is obtained from the ionization continuum with corrections for the acceptance angle given by Eq. (1), assuming an isotropic scattering.

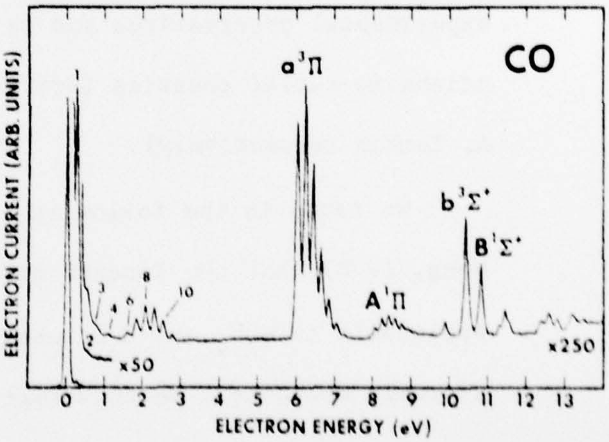

FIG. 24. Constant residual-energy spectrum of CO at near zero residual energy.

Wing-Cheung Tam and S. F. Wong, Rev. Sci. Instr. 50, 302 (1979).

Figure 24 shows the capacity of the present apparatus for threshold vibrational and electronic cross section studies. The lowest usable impact energy is essentially limited by the apparatus resolution (presently 55 meV). We expect that further refinements in design should make possible the study of inelastic processes down to thermal energies. At present most of the work is in this energy regime and mainly by swarm experiments.

C. Dissociative Attachment From Excited Molecules

This is a new program we developed in the last half-year of 1978. The main goal is to study the explicit role of initial vibrational and rotational (in some cases) states on dissociative attachment cross sections. Experimentally, this is achieved by studying the negative ion formation cross sections from hot molecules with resolution of initial excited states. Before the conclusion of the 1975-1978 program we completed the first study of H_2 and D_2, two basic prototype molecules. A marked dependence of H^-/H_2 and D^-/D_2 cross sections on initial vibrational ($v = 0 - 5$) and rotational ($j = 0 - 7$) states was observed. Figs. 25 and 26 show the highlights of our results.

Our experiments in the 3.75 eV resonance region show that there is a ten-fold increase in H^- cross section with each increase in vibrational quanta yielding a cross section $\sim 10^{-16}$ cm^2 for $v = 4$. We also noted that the role of rotational states, while large, was less drastic compared with vibrational states for the same internal energy.

Using a resonant theory, Wahedra and Bardsley (1978) were able to account for our findings (theory in Fig. 26) with the much disputed $^2\Sigma_u^+$ compound state. Thus we consider the present work adds much ground to the

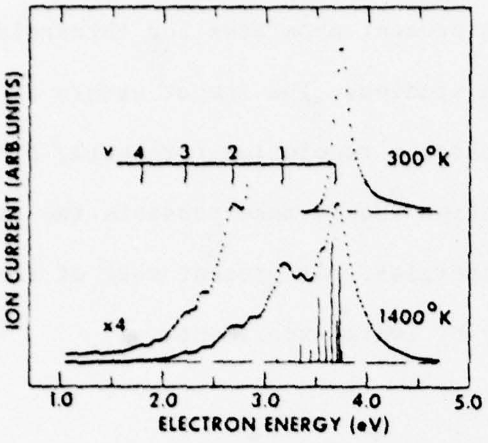

FIG. 2 5. Threshold region of H^-/H_2 *cross-section* curves at 300 and 1400°K. Note that in the 1400°K curve, peak intensities from excited molecules are much larger than expected from the vibrational population (e.g., 1.4% *for* $v = 1$) *and rotational* population (vertical bars), reflecting a drastic increase of cross section with vibrational and rotational quanta.

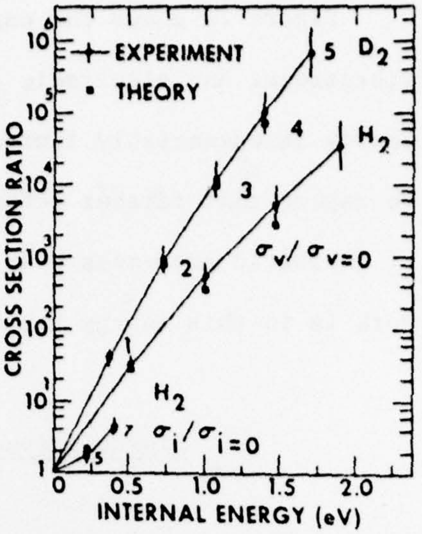

FIG 2 6. Internal-state dependence of threshold dissociative attachment cross sections in H_2 and D_2 via the $^2\Sigma_u^+$-shape resonance. *The ground-state* cross sections (300°K) are 1.6×10^{-21} cm^2 for H_2 and 8×10^{-24} cm^2 for D_2

M. Allan and S. F. Wong, Phys. Rev. Letters 41, 1791 (1978).

existence of this very short-lived resonance (e.g. see G. J. Schulz, 1973).

In experiments on nuclear fusion via magnetic confinement, one tries to heat a plasma with an intense beam of neutral H and D atoms. At high injection energies such beams are more efficiently produced by stripping H^- and D^-, thereby requiring an intense source of hydrogen negative ions (e.g. see Prelec, 1977). The present findings appear to provide a new mechanism for such ion production and an explanation for the anomalous H^- density recently observed in a H_2 plasma (Nicolopoulou, Bacal and Doucet, 1977; Hicks, Bacal, and Hamilton, 1979).

V. PERSPECTIVES: PAST AND FUTURE

In this Section we give a perspective of our ARO Program during 1972-1978 and an outline of further work that is the logical outgrowth of this program based on our expertise developed over the years.

A. Perspectives of the Past Program

Our research in the 1972-1975 period was centered around triatomic and diatomic systems of atmospheric interest. We consistently found that vibrational excitation proceeded predominantly via resonant processes existing in those systems with strong triatomic dipole moments. The most fruitful studies of resonances in molecules were done by measurements of the vibrational excitation.

As a result of the above work, we developed a hydrocarbon program in the 1975-1978 period. Through three different experiments discussed in Section IV, we found that the general lessons we learned from diatomic and triatomic molecules were equally applicable to prototype hydrocarbon molecules such as C_6H_6, C_2H_4, etc. In addition, unexpected regularities were observed, traced to the symmetry properties of these systems. Specifically we would like to quote the concluding paragraphs from our ethylene paper.

> We find that the general features in energy-loss spectra and in energy and angular dependences of vibrational cross sections in ethylene can be understood using (i) the resonant orbital and partial wave concepts developed for simpler systems, together with (ii) the recently postulated[3] selection rules. We find also that (iii) the role of resonance lifetime is important in vibrational excitation and the general conclusions of the boomerang[14] (intermediate lifetime) and impulse-limit[22] (short lifetime) theories provide useful insights for interpretation. These point the way to the unraveling of the energy transfer processes in electron collisions with other complex molecules.

> The resonant vibrational excitation observed in prototype hydrocarbons, benzene and ethylene, seems remarkably sensitive to the symmetries of the orbitals and nuclear motion of the molecules. For example, in the second resonance region of C_2H_4, the incident electron excites predominantly a single vibrational mode ν_1 over a broad energy range (~ 4 eV). Similar findings are expected in other hydrocarbon molecules; this may lead to better understanding of infrared lasers involving gas discharges. The present study also demonstrates the potential of the present experimental approach for exploring the energy locations and symmetries of low lying unoccupied molecular orbitals.

I. C. Walker, A. Stamatovic, and S. F. Wong,
J. Chem. Phys. 69, 5532 (1978).

We have also completed experiments on the prototype molecules CH_4 and CD_4 since 5 June 1978 when we submitted a renewal proposal to ARO. The official ARO decision on 10 April 1979 not to renew funding this ongoing program interrupted its publication.

B. Suggested Further Work

As is our tradition we developed experimental capability for two new lines of research during the 1975-1978 period, namely an electron impact spectrometer for very low impact energies and dissociative attachment studies with resolution of initial vibrational states. Below we present our view of research lines to take advantage of these accumulated efforts, if new funding becomes available.

In vibrational excitation we consider the time and experimental techniques are ripe for a comprehensive study of a selected number of small molecules. In order to form a global view of the excitation mechanisms, we will direct our efforts toward differential and total cross section measurements with impact energies extending both above ionization limits to 30 eV and down to the threshold regions near 0.2 eV. Very little information is available in these two regions (e.g. see G. J. Schulz, 1976; D. G. Truhlar et al., 1977). Fig. 27 shows our initial results of large-energy-scale studies of N_2. The new resonant regions in addition to those studied earlier are observed. In addition to a basic interest, we also consider that the large energy-integrated cross sections ($\sim 10^{-16} cm^2$ eV) contributed by the very broad resonance near 22 eV provide an efficient vibrational excitation by fast electrons in certain energy ranges. Regarding threshold vibrational excitation, the present beam studies have been largely confined to hydrogen halides (F. Linder, 1979). The theoretical understanding is far from unique, for example both virtual states (L. Dubé and A. Herzenberg, 1977) and resonance interpretations (H. S. Taylor et al., 1977) have been invoked for the threshold peak in HCℓ. Further experimental information in nonpolar molecules will be helpful in elucidating the threshold excitation processes (M. A. Morrison et al., 1977; N. F. Lane, 1977).

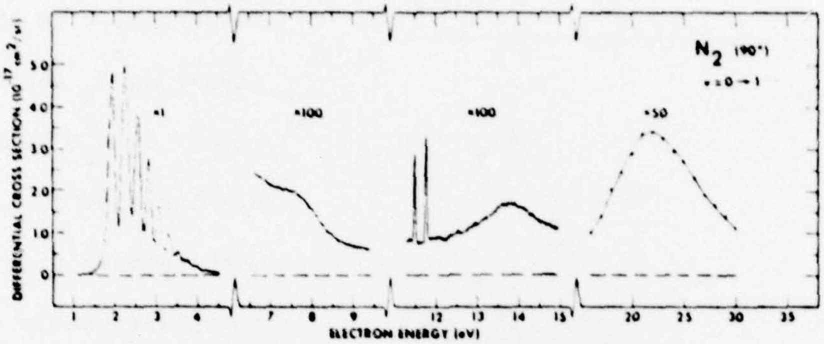

FIG. 27. Global view of vibrational excitation in N_2 to v = 1 in the energy range 1 - 30 eV.

S. F. Wong and G. J. Schulz, unpublished.

Recent work by Rohr (1978) on more complex nonpolar molecules such as SF_6 have observed strong threshold peaks in vibrational excitation. We visualize CO and CO_2 as the two good starting molecules.

Another line of research we would like to pursue is dissociative attachment from <u>vibrationally excited molecules</u>. Previous experiments by Henderson, Fite and Brackmann (1969) on O_2 and by Chantry (1969) on N_2O have shown a big increase in cross sections with temperatures attributable to vibrationally excited molecules. Fig. 28 shows the results of O^-/O_2 as summarized by H. S. W. Massey (1976) as an illustration. Our recent improvements in our ion-optics design and excited-molecule production has made possible the first resolution of initial vibrational and selected rotational states.

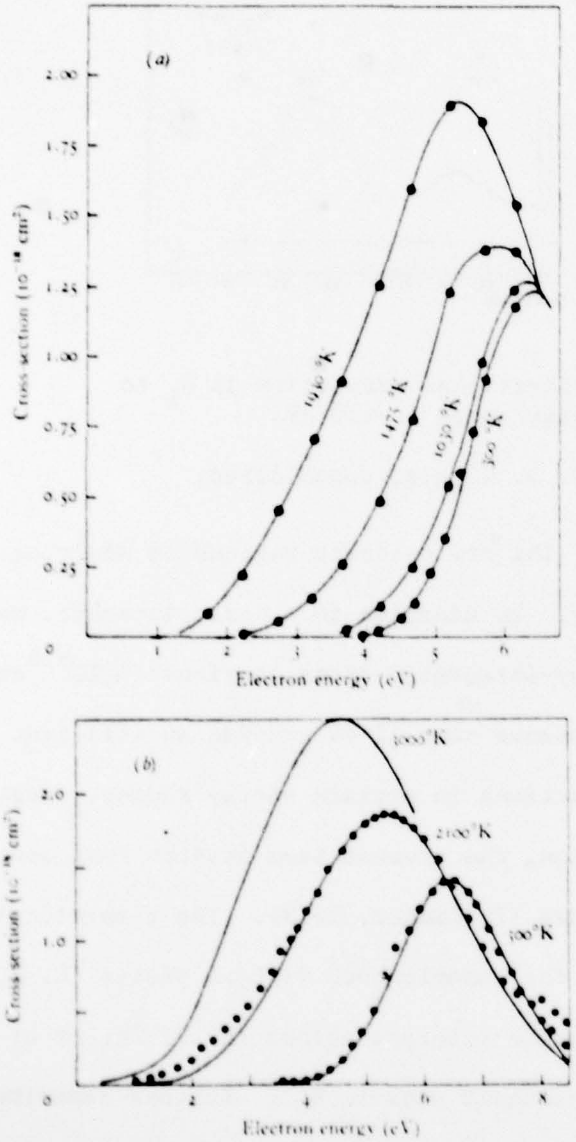

Fig. **28.** Total cross-sections for dissociative attachment of electrons to O_2 as function of electron energy for different gas temperatures as indicated. (*a*) -● ●- observed by Henderson *et al.* (1969); (*b*) —— calculated by O'Malley (1967), ● observed by Fite and Brackmann (1963).

<u>Negative Ions</u>, H. S. W. Massey, Cambridge University Press, 1976, p. 322.

Figs. 29 and 30 show our initial results on H_2 and D_2. We would like to extend these studies to HCℓ and HF at low energies. In addition to basic information on dissociative attachment from excited hydrogen halides, we also expect the results will shed light on the mechanism responsible for threshold vibrational excitation:virtual states or regular resonance.

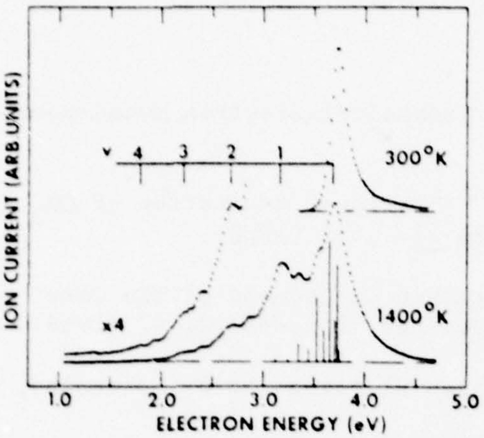

FIG. 29. Threshold region of H^-/H_2 cross-section curves at 300 and 1400°K.

M. Allan and S. F. Wong, Phys. Rev. Letters 41, 1791 (1978).

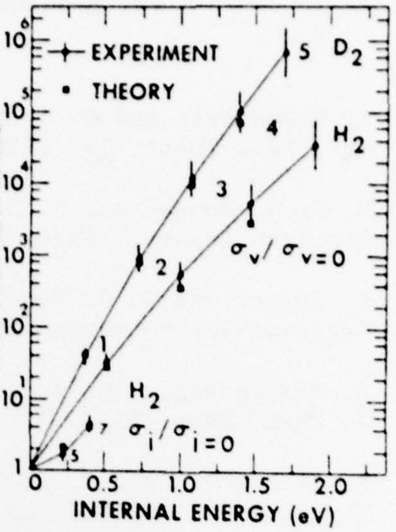

FIG. 30. Internal-state dependence of threshold dissociative attachment cross sections in H_2 and D_2 via the $^2\Sigma_u^+$-shape resonance.

Acknowledgement

We would like to thank ARO for the support of our electron impact program at Yale during the years 1966-1978. We are particularly grateful to ARO for the uninterrupted support since the death of George J. Schulz, the former principal investigator, on January 15, 1976. This, together with other timely help, enabled us to establish the proposed hydrocarbon program, as well as to develop new experimental capabilities for future research.

VI. PUBLICATIONS UNDER ARO SPONSORSHIP

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