

COLLISIONAL-ELECTRON DETACHMENT OF Cl⁻ ON DIATOMIC MOLECULES

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Recent experimental results for collisional-electron detachment of Cl⁻ by H₂/D₂, N₂, O₂, NO, and CO are discussed. The emphasis is on angular distributions and energy loss measurements for laboratory energies of a few hundred eV. Evidence for the possibility of bound excited states of N₂Cl and COCl and the role of target negative-ion resonant states is presented.

INTRODUCTION

Much of the collisional electron detachment work which has been published since the last ICPEAC has been concerned with the collisions of negative atomic ions and atomic targets, and the intricacies of this work could well be the subject of a progress report. However, it will have to suffice to say that the question of appropriate theoretical analysis of these supposedly simply systems is not yet fully resolved.¹ Despite the difficulties or perhaps because of them, there has been a shift in emphasis--at least on the part of experimentalists--to molecular targets, and much of this work has only just become available at this meeting. A synthesis of all the new material is beyond the scope of this report which instead will be concerned primarily with our work at Oak Ridge National Laboratory on detachment of Cl⁻ by the common atmospheric diatomic targets at sub-keV projectile energies as well as the closely related work of Champion, Doverspike, and co-workers at the College of William and Mary.

The interest in the detachment behavior of Cl⁻ is due in part to the high electron affinity of chlorine. As a result, the orbital velocity of the attached electron is greater than the relative collision velocity of a typical collision pair until projectile energies on the order of a few kilovolts are reached. Consequently, at lower energies a quasi-molecular description ought to be applicable. At the opposite extreme of the electron affinity scale, H⁻ for example, the orbital velocity of the extra electron will often be less than typical collision velocities and so the scattering may more closely resemble that of a free electron. A considerable variation in the collisional detachment for arbitrary systems is thus to be expected.

Three types of detachment processes are of interest for the systems we have studied. These are

- Cl⁻ + AB → Cl + AB + e (1)
- Cl⁻ + AB → Cl + AB* + e (2)
- Cl⁻ + AB → Cl + AB⁻ (3)

MASTER

Reaction (1) is the so-called "simple" or "direct" detachment process and corresponds to the direct emission of the electron from the projectile accompanied only

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by rotational/vibrational excitation of the target. This process is most analogous to detachment by an atomic target. As indicated above, the best theoretical description for this type of detachment is still an open matter.¹ However, at the relatively low collision velocities of the present study the local complex potential model² should provide a useful framework for discussing detachment collisions. This same model has been successfully applied to the related processes of Penning ionization³ and associative/dissociative attachment,⁴ and the physical picture resulting from this model is diagrammed in Fig. 1.

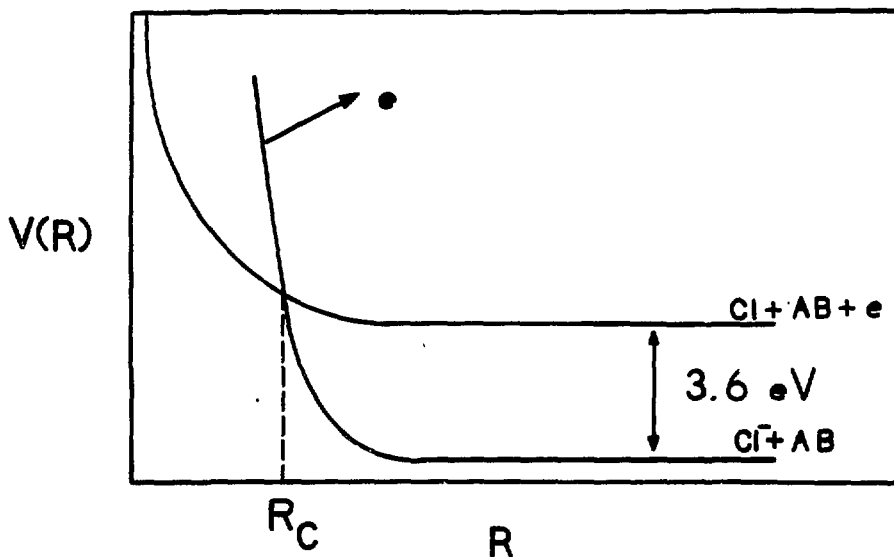


Figure 1
Complex Potential Model

The potential curve appropriate to the ion-neutral interaction is assumed to cross that for a neutral-neutral interaction at some value of the internuclear separation R_C . The latter potential curve actually represents the lower limit of a continuum of states corresponding to the heavy particles and a free electron. For a sufficiently small impact parameter the colliding particles will penetrate to values of R such that $R < R_C$, but in this region there will be a finite probability that the electron will be ejected and carry off an amount of kinetic energy equal to the difference in the two potentials. In principle, at a given value of R , an electron may be emitted on the inward part of the trajectory or remain attached until the turning point is reached and be emitted on the way back out. In either case the K.E. of the electron will be the same but the heavy particles will experience different trajectories and structure may appear in the differential cross section. Figure 1 shows potential curves which are purely repulsive with a crossing point corresponding to a value of the energy exceeding the electron affinity of Cl. This is justified by the recent results of Doverspike, et al.,⁵ who established that the thresholds for several of the collision pairs of interest to us do indeed exceed the electron affinity by 1-4 eV.

Reaction (2) can be incorporated in this picture, at least in a qualitative sense, since there will also be a potential curve appropriate to the interaction of neutral chlorine and the target molecule in an electronically excited state. The trajectories of the scattered heavy particles will then reflect the relative probabilities of electron emission due to the crossings with the ground and excited state potentials.

Reaction (3), the charge transfer process, is complicated by the fact that for

the diatomic targets so far considered the negative molecular product ion is typically a resonant state with a lifetime of 10^{-15} to 10^{-10} sec. Evidence for the formation of such a resonant state was obtained by Risley⁶ in an analysis of the electron spectrum produced by collisions of H^- and N_2 ; however, the degree to which this channel was involved in the detachment collisions was not clear. One of the objectives of our study was to determine if there was evidence for such an occurrence in other systems.

The total cross section data (along with the results for related rare gas⁷) for some diatomic⁵ targets obtained by the William and Mary group has been plotted in Fig. 2 as a function of relative kinetic energy. For the low energies shown, no particular structure is evident and the limited amount of data at higher energies indicate that the cross sections slowly increase until energies in the keV range are reached. As an example, at 14 keV the detachment cross section for Cl^-/CO increases to about $45 A_0^2$ and does not decrease until approximately 50 keV.⁸ No particular pattern is as yet obvious from the threshold results which established values in the range $4\frac{1}{2}$ to $5\frac{1}{2}$ eV for H_2 , D_2 , and O_2 and $7-7\frac{1}{2}$ eV for He, Ar, N_2 , and CO.

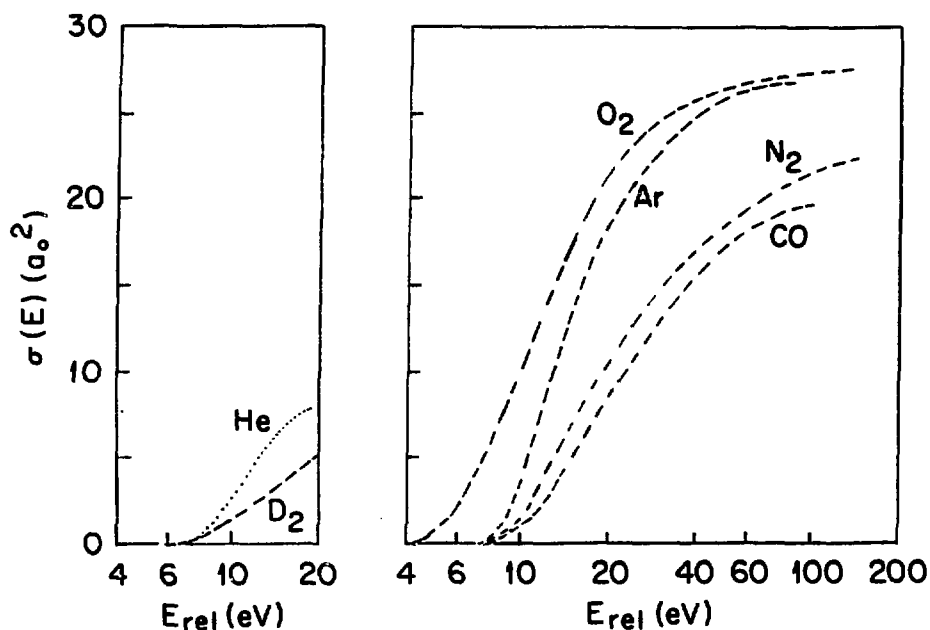


Figure 2
Total Detachment Cross Sections of Cl^- in Various Gases

The initial effort at Oak Ridge to characterize detachment from Cl^- by diatomic targets was a determination of the energy losses of the neutralized chlorine product resulting from collisions with D_2 and H_2 .⁹ The experiment involved the use of time-of-flight methods. The complexities of energy loss involving molecular targets are more readily put in perspective by comparison with a closely related rare gas target. In this case the kinematic effects are identical in both systems and do not obscure such a comparison. The energy loss spectra for Cl resulting from a collision with He at a scattering angle of 1° and projectile energy of 350 eV is shown in Fig. 3.

For the He target only "simple" detachment is observed with an energy loss of 4 eV which corresponds to the minimum endothermicity of 3.6 eV (E.A. of Cl) plus a few tenths of an eV kinetic energy of the ejected electron. The energy loss spectrum for a D_2 target at the same energy and scattering angle is shown in Fig. 4.

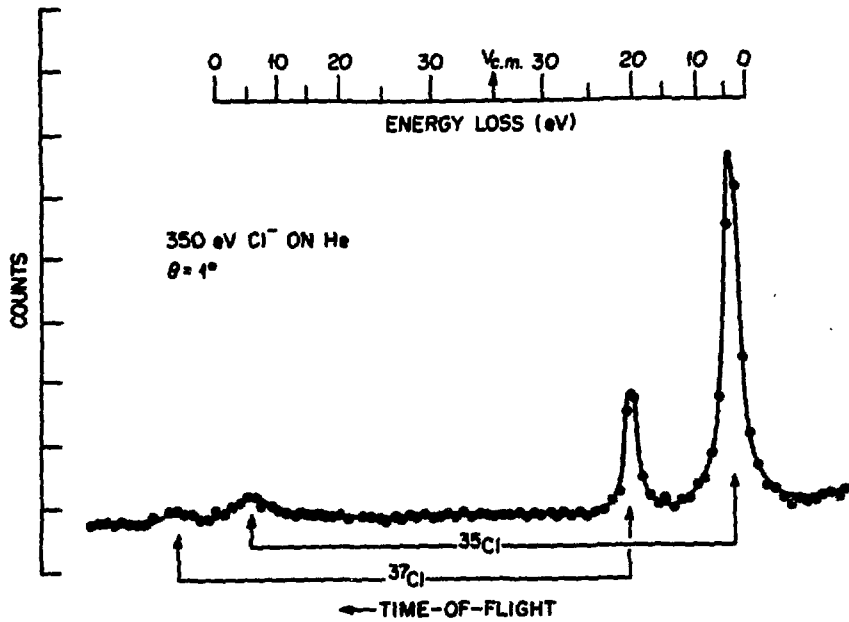


Figure 3
 Energy Loss Spectrum on Detachment Collisions with He;
 Peaks at left are caused by back scattered (in C.M.) particles

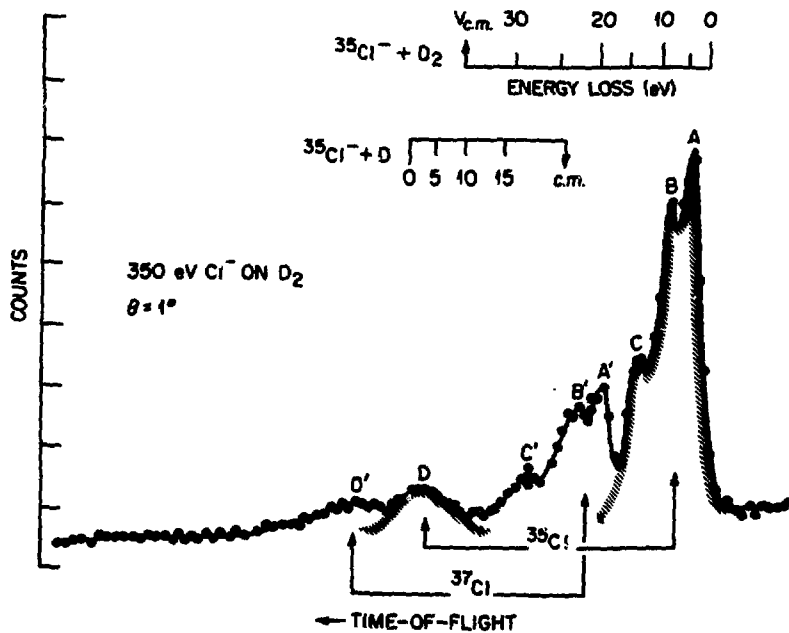
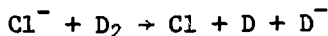


Figure 4
 Energy Loss Spectrum of Cl^0 Formed by Detachment with D_2

Although the dominant peak (A) in the spectrum is essentially identical to that for He, two additional channels labelled B and C are readily apparent. The energy loss of peak B corresponds to dissociative attachment of D_2 , i.e.,



or



Peak C is ascribed to an electron transfer to the $2^2\Sigma_g^+$ resonance of H_2^- which is a repulsive state and also ultimately leads to dissociation. Peak D corresponds to the backscattered contribution arising from simple detachment and is the equivalent to Peak A for small impact parameter collisions. No isotope effects were observed in this study so that the preceding comments also apply to an H_2 target.

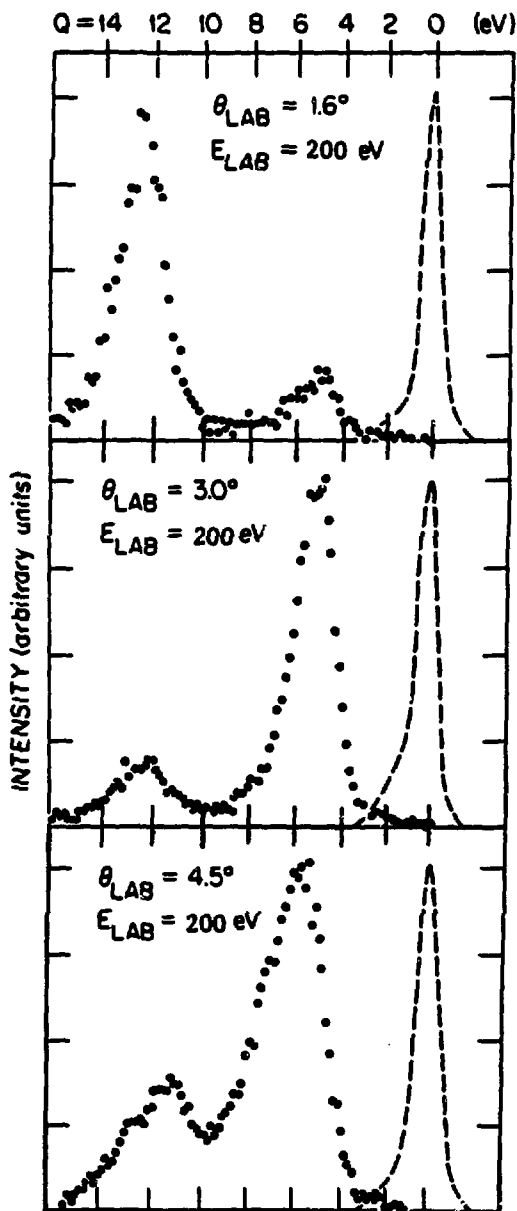


Figure 5
Energy Absorbed (Q) in Detachment Collisions with N_2 Target

In the Cl^- and N_2 system the maximum scattering angle is $\sim 3^\circ$ and differential measurements are difficult. As the mass of the target molecule is increased, the kinematic constraints are relaxed and it was possible to measure energy losses and scattered intensity as a function of angle. Such measurements required an apparatus with provision for scanning a wider angular range than was available with that used in the hydrogen experiments. Consequently a second apparatus which incorporated basically the same ion source and time-of-flight techniques was developed. The angular resolution was 0.5° , a scattering cell was used, and beam energies were 150, 200, and 300 eV.

A sample of the data¹⁰ for a nitrogen target for a laboratory beam energy of 200 eV is shown in Fig. 5 for various angles. An illustration of the apparatus energy resolution is provided by the spectra for the elastic scattering of Cl^- by argon which are shown as dashed peaks. Two energy loss peaks in the N_2 data are clearly resolved which correspond to losses of approximately 6 and 12 eV. As with D_2 and He , it is useful to make a comparison between N_2 and Ar . The kinematics are similar for the latter targets but unlike N_2 the only feature in the detachment energy loss spectrum for an argon target was a peak centered in the range of $4-4\frac{1}{2}$ eV. At an angle of 4.5° the full width at half maximum of the argon peak was less than half that shown for N_2 .

The remarkable feature of this data is that at the lowest scattering angles a high energy loss channel dominates the detachment process. Although scattering data on related systems is rather limited there is no indication that high energy loss low angle scattering is to be expected. For example, Inouye, et al.,¹¹ have done energy loss measurements on the isoelectronic system $\text{K}^+ + \text{N}_2$ and Fernandez, et al.,¹² have obtained energy loss data for $\text{Ar}^+ + \text{N}_2$. In both experiments energy loss peaks which, when the E.A. of Cl is taken into account, correspond roughly to our 12 eV peak, but this peak was present only at larger values of ($\tau \approx E\theta$) while the low angle scattering was dominated by quasi-elastic processes. In addition, Champion and Doverspike¹⁰ measured the inelastic losses associated with the non-detaching channel for $\text{Cl}^- + \text{N}_2$ and found no evidence for a high-loss peak. Consequently, it would appear that there is something unique about the detachment channel.

The most probable energy loss (Q) for several beam energies are plotted as a function of τ in Fig. 6. The 12 eV loss channel varies with τ in a manner markedly different from that for the 6 eV channel. Furthermore, if the τ dependence of the high energy loss channel for the K^+/N_2 and Ar^+/N_2 systems were plotted in this manner, in both cases the Q value would show an increase with τ rather than the decrease shown in Fig. 6. The energy losses appropriate to detachment accompanied by target excitation are shown on the right-hand ordinate. The most likely candidates for the 12 eV channel appear to be excitation of the $a^1\Pi_g$ and the $a'^1\Sigma_u^-$ states of N_2 or charge transfer to the N_2^- resonances labelled "a" and "a'".¹³ The peculiar τ dependence of this channel strongly suggests that more than one electronic excitation is involved since excitation of a single level is expected to increase with scattering angle as vibrational-rotational excitations of the excited state occur.

Formation of the autodetaching state of Cl^- observed by Cunningham and Edwards¹⁴ is discounted because the energy losses at high τ are too small, and at lower τ values we found no evidence for this channel with other targets (with the exception of CO). In addition, separate experiments were carried out with F^- and the same 12 eV energy loss peak appeared. Excitation of the analogous auto-detaching states of F^- should require an energy loss of approximately 16 eV.

The low energy loss channel (5-7 eV) shown in Fig. 6 is appropriate (within the experimental uncertainty) to the formation of the $2^1\Pi_g$ resonant state of N_2^- . The relative differential cross sections for each of the two channels are given in Fig. 7. The low-loss channel can be seen to dominate the scattering in the

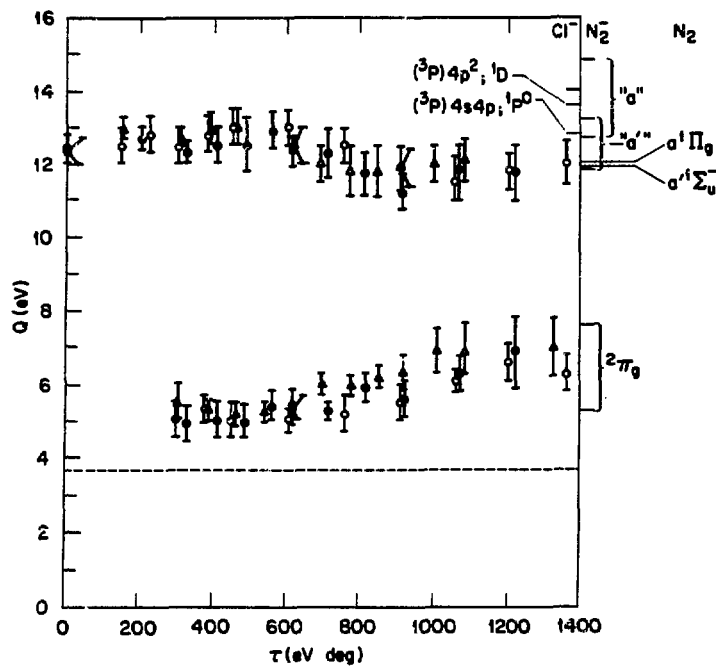


Figure 6
Energy Loss, Q , in Detachment Collisions of $(\text{Cl}^- + \text{N}_2)$ vs τ

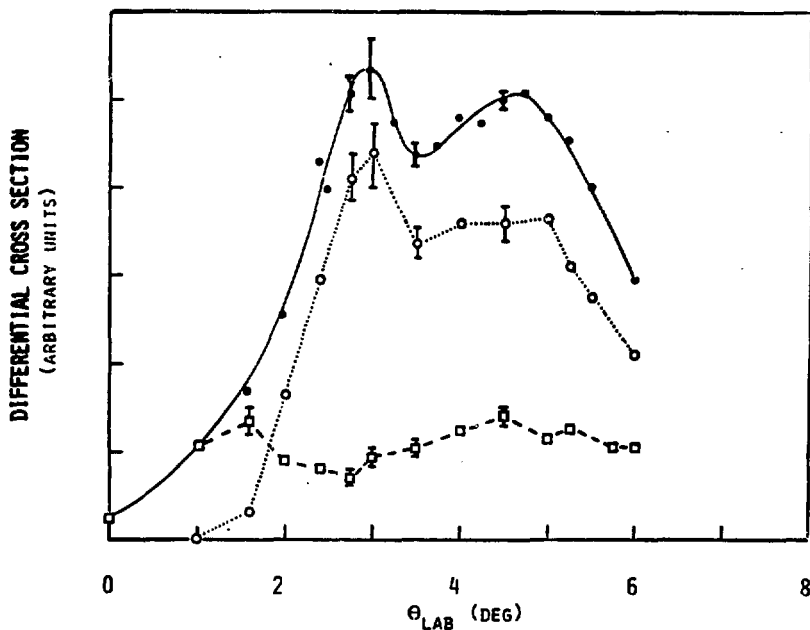


Figure 7
Differential Cross Section for Cl^0 Formed in Detachment Collisions with N_2 at 200 eV (Lab). Low-loss Channel, \circ ; high-loss channel, \square .

intermediate ranges of angles and to pass through a local minimum at 650-700 eV deg. The high-loss channel also has a local minimum at about 500 eV-deg. Similar structure was also observed at a nominal beam energy of 150 eV¹⁰ while at 300 eV only a hint of the minimum in the high-loss channel was observed.

Energy loss measurements with CO as a target produced results qualitatively similar to those for N₂, i.e., two energy loss peaks were clearly resolved and within experimental uncertainty the Q vs τ behavior of the low loss channel was found to be indistinguishable from that shown in Fig. 6. As was the case for N₂, this energy loss is also commensurate with charge transfer to a ² Π resonance of CO⁻. In addition, the Q values for the high loss channel were observed to be \sim 11.5 eV at low τ and unlike N₂ increased slowly to about 13 eV. CO has fewer excited states than N₂ and no resonances in the appropriate energy range. The 11.5 eV threshold appears to be most appropriate to excitation of the A ¹ Π state of CO. As with N₂, the energy loss spectra obtained in some F⁻/CO experiments lead us to conclude that target rather than projectile excitation dominates the scattering.

The relative angular differential data for a 200 eV (Cl⁻) beam in CO is shown in Fig. 8. Like N₂, CO targets produce significant high-loss, low-angle scattering. However, the angular intensity variation for both channels is more extreme for CO. The same type of structure was also found in the data for beam energies of 150 and 300 eV.

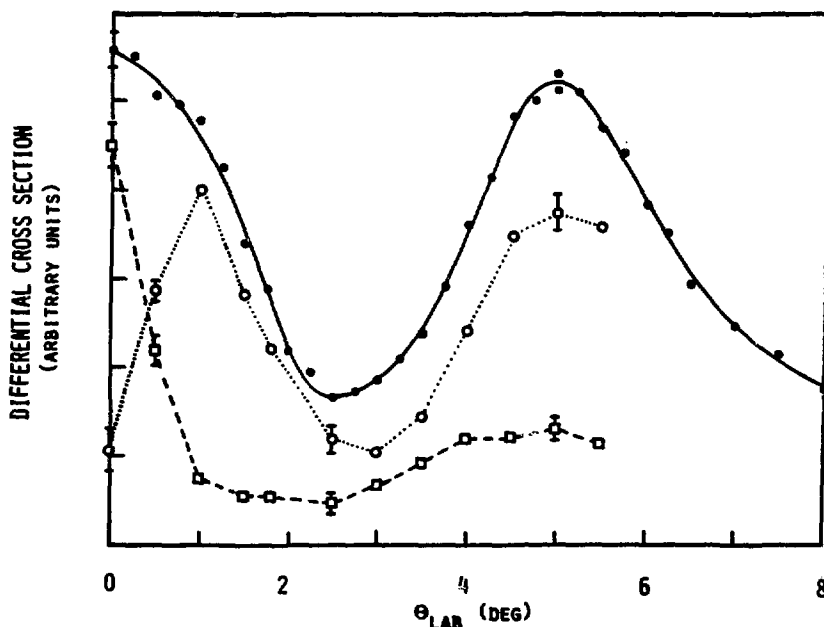


Figure 8

Differential Cross Section for Cl⁰ from Collisions of Cl⁻ with CO at 200 eV (lab.)

Representative loss spectra for NO and O₂ targets at beam energies of 200 eV (lab.) are shown in Fig. 9. Unlike the N₂ and CO data, the results for NO and O₂ show no indication that high energy loss channels play a role in the low angle scattering. In the case of NO, as the scattering angle is increased it is apparent that another channel with an energy loss of about 12 eV does begin to contribute to detachment.

Both the magnitude of the most probable Q value for the dominant channel in the NO scattering (5-7 eV) and the τ dependence of Q closely resembles that for N₂ and CO; consequently there is no evidence for charge transfer to the stable ground vibrational state of NO⁻(³ Σ^-). Evidence for ¹ Δ and ¹ Σ^+ resonant states of NO⁻ in the range 0.7 \sim 2.5 eV have been found in electron impact experiments by Tronc, et al.,¹⁵ and charge transfer from Cl⁻ to these states might contribute to our observed energy losses.

The most probable Q value for detachment by O₂ at low scattering angles is about

4 eV (Fig. 9). Charge transfer to a bound state of O_2^- would give rise to an energy loss in the 3.2 to 3.6 eV range; hence, if the $X^2\Pi_g$ state of O_2^- is involved, our measurements indicate that it would have to be through an autodetaching vibrational level. The scattered intensity at a laboratory angle of 1.0° is quite low and this is responsible for the ragged appearance of the high energy loss side of this spectrum. However, as the scattering angle is increased to 4.0° , intensity is no longer a problem and it is quite clear that a second channel opens. It is not clear as to whether or not the process giving rise to the 4 eV peak at 1.0° is the same process causing the peak of ~ 4.2 eV at 4.0° . At the latter scattering angle we also observed an energy loss of about 4.2 eV with an argon target; consequently, in this case the energy loss measurements are insufficient to unequivocally identify the detachment channel.

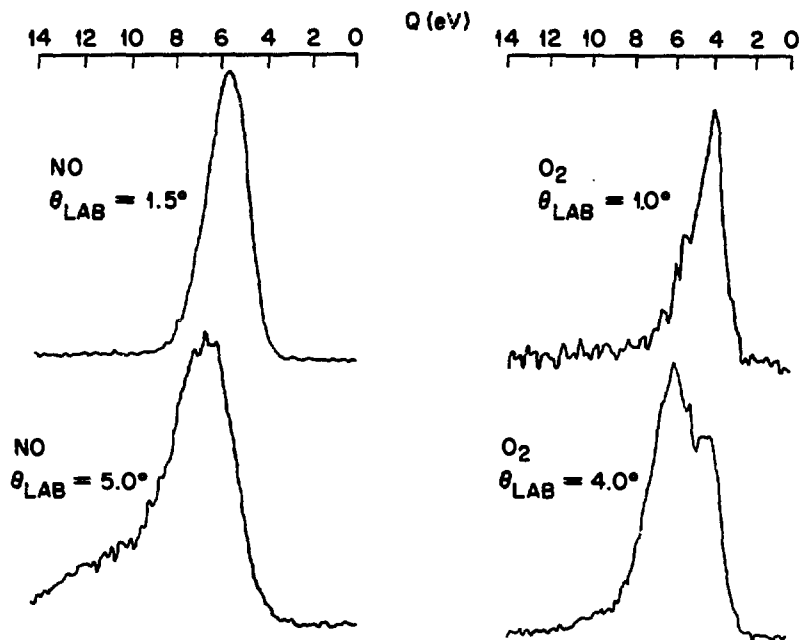


Figure 9
Energy Loss Spectra for NO and O_2 at 200 eV (lab.)

Despite the structure in the energy loss measurements for O_2 , the angular differential cross section proved to be featureless (Fig. 10) in contrast to that observed for the other targets. The differential cross section for a laboratory energy of 200 eV for Cl^- on NO is also shown in Fig. 10. Although it is difficult to unambiguously separate the relative contribution of the high-loss channel which the TOF spectra indicate is present at larger scattering angles, comparison of the spectra for NO and O_2 in the Q range of 8-14 eV suggests that the shoulder at about 7° in the NO data of Fig. 10 can be interpreted as structure in the low-loss channel.

DISCUSSION

The data presented here are sufficient to demonstrate that collisional electron detachment by the simple diatomic molecules H_2 , N_2 , NO, O_2 , and CO proceeds in a complicated and highly specific manner. Within the framework of the local complex potential model it is apparent that several potential surfaces and electron ejection probability functions are necessary for each molecule in order to account for the observations. In general this material is not yet available; however, in

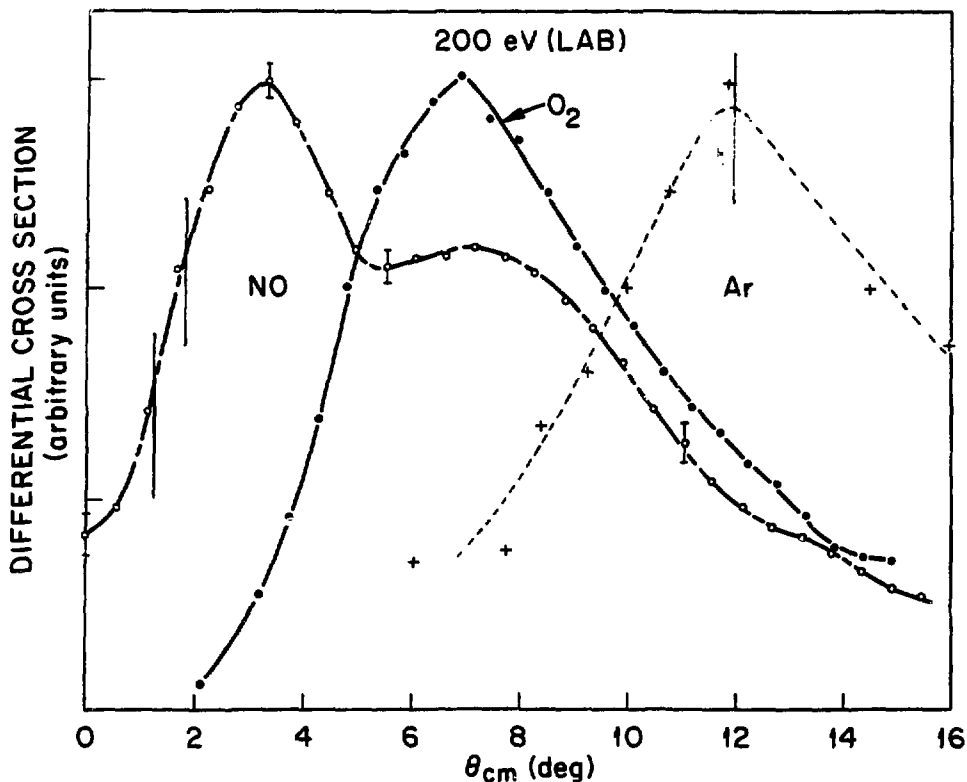


Figure 10
Differential Cross Sections for NO, \circ , \bullet ; and Ar, +, at 2000 eV (lab.)

the case of $\text{Cl}^- + \text{NO}$ and $\text{Cl}^- + \text{Ar}$ there is some information on the potential that may be useful in providing an insight into the difference in differential detachment cross sections for these collision pairs. As may be seen in Fig. 10 where a differential cross section for $\text{Cl}^- + \text{Ar}$ collisions based on the work of Fayetteon, et al.¹⁶ has been plotted, the detachment scattering for NO occurs at substantially smaller angles than that with an argon target.

NO and Cl form a stable, bent molecule which has a well depth of 1.6 eV¹⁷ along the N-Cl axis, and by fitting a Morse potential to some of the spectroscopic data¹⁸ we have generated the NOCl curve shown in Fig. 11. First approximations to the $\text{Cl}^- + \text{NO}$ potential are provided by the potentials for the isoelectronic systems $\text{K}^+ + \text{NO}$ and $\text{Ar} + \text{NO}$. The former was obtained from elastic scattering¹⁹ and the latter comes from the electron gas calculations of Nielson, et al.²⁰ Appropriate projections of the potentials along the N-Cl axis have been used and it is apparent from Fig. 11 that the potentials for the incoming part of the trajectory intersect the NOCl curve near the minimum in the attractive well. This is in marked contrast to the potentials for $\text{Cl}^- + \text{Ar}$ and $\text{Cl} + \text{Ar}$ as calculated by Olson and Liu²¹ and also shown in Fig. 11. These potentials are purely repulsive and cross at about 6.5 eV. With these potentials we can now make an estimate of the threshold or minimum scattering angle for a detachment collision. In such a case the electron is ejected with zero kinetic energy at the crossing point which also serves as the turning point in the heavy particle trajectory. The resulting threshold angles are given by vertical lines in Fig. 10. The threshold angle for Cl^- with Ar proves to be an overestimate, but the threshold data⁷ suggest that the crossing point of the potential should be reduced by 3 eV which should bring the threshold angle into better agreement with the experimental data. However, the point is that these approximate calculations strongly suggest that in order to further reduce the scattering angle to the range appropriate to Cl^-/NO

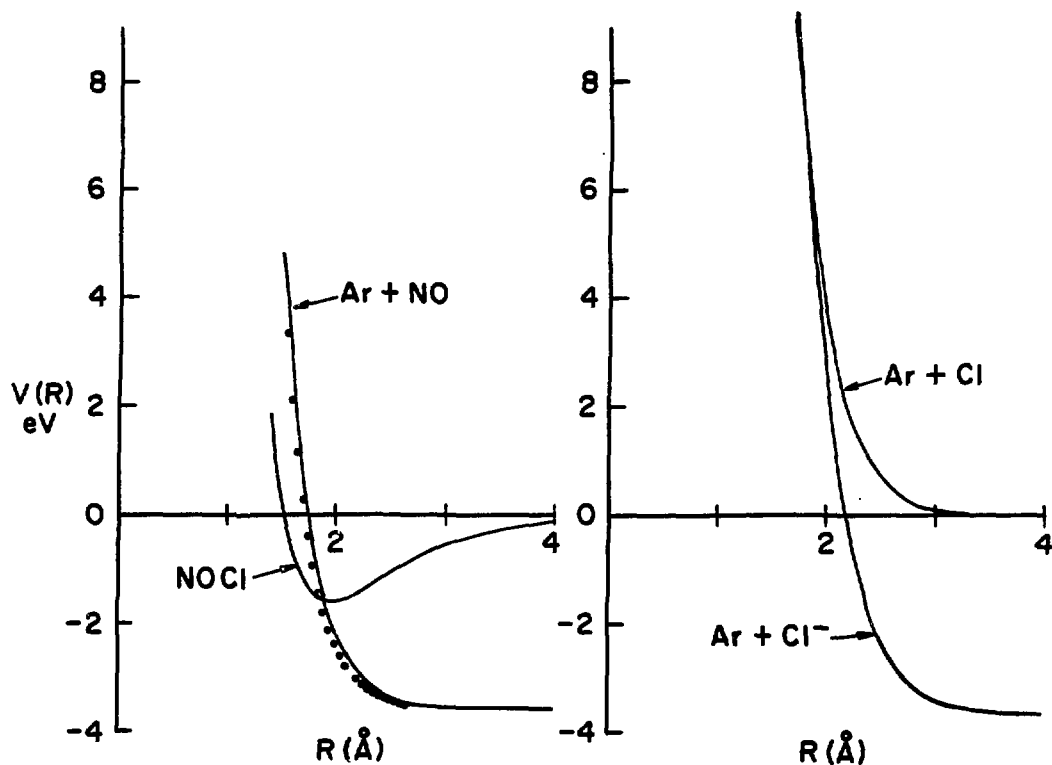


Figure 11
Potentials. (\cdots shows $\text{K}^+ + \text{NO}$.¹⁸)

it is necessary to have curve crossing in an attractive region of the exit channel. The energy loss measurements near the forward direction with an NO target show that an endothermicity of some 5 eV is involved whereas in the above calculation the appropriate value is 3.6 eV. If the threshold process corresponds to "simple" detachment accompanied by vibrational-rotational excitation then the additional energy loss should further reduce the threshold angle to give even better agreement with the observations. As discussed above, the energy losses are also in accord with formation of NO^- resonances. If the threshold process corresponds to charge transfer, then the forward scattering implies that at some angle of attack there must be a minimum in the $\text{Cl} + \text{NO}^-$ surface.

If we now reconsider the observations of the low-angle, high-loss scattering with N_2 and CO , the same type of threshold angle calculation suggests that a bound excited state such as that sketched in Fig. 12 ought to be able to account for the low angle scattering. The "black box" area shown in Fig. 12 indicates that there is too little information to order the curves in this region. Since the outer shell of O^- is isoelectronic with neutral chlorine, we have included in Fig. 12 a simplified representation of N_2O^- bent at an angle of 125° . This is based on the adiabatic correlation diagram of Krauss, et al.²² (A similar diagram is also appropriate for $[\text{CO}_2^-]^*$ which is the analog of $[\text{COCl}]^*$.) Since no stable ground of N_2Cl is known to exist, consideration of Fig. 12 suggests the possibility that low energy associative detachment collisions could populate an excited state which might then radiatively dissociate in a manner analogous to the rare gas-halogen excimers. A second generation of experiments at lower energies involving spectroscopic product analysis and/or or a search for backscattered metastable product should help to determine the nature of the excited state.

One of the objectives of this survey was to determine the evidence for the involvement of the negative ion resonant states of the targets. Detachment by charge

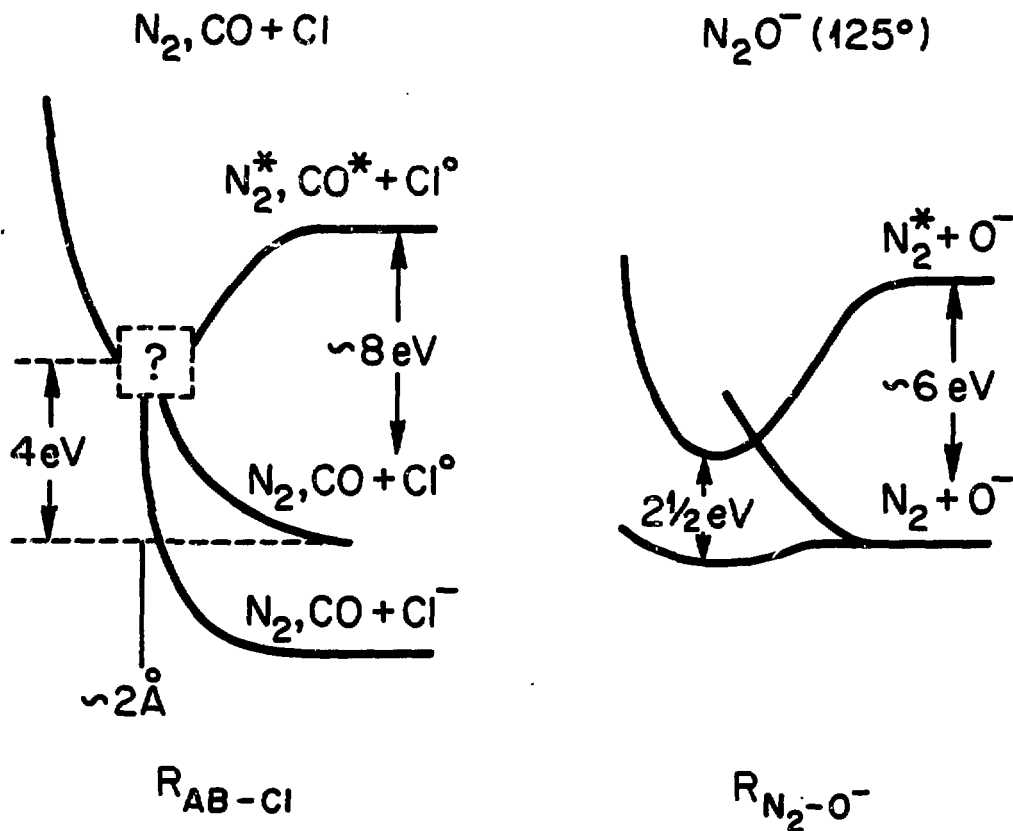


Figure 12
Schematic Potential Curves

transfer should result in an energy loss rather different from that for "simple" detachment. For N_2 , CO , and NO , the observed energy losses are consistent with charge transfer. However, there do not appear to be any unambiguous arguments for discounting the possibility that the energy losses are in part attributable to "simple" detachment accompanied by vibrational-rotational excitation. This is in contrast to the results of Tuan and Esaulov²³ for detachment collisions of H^- and N_2 and CO where definite structure which could be attributed to the charge transfer and "simple" detachment channels is apparent. In the case of the more tightly bound Cl^- , experiments involving measurement of the electron spectra might resolve the matter.

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REFERENCES

- [1] de Vreugd, C., Wijnaendts van Resandt, R. W., Delos, J. B., and Los, J., *Chem. Phys.* [to be published].
- [2] Mizuno, J., and Chen, J.C.Y., *Phys. Rev. A*4 (1971) 1500-1516.
- [3] Miller, W. H., *J. Chem. Phys.* 52 (1970) 3563-3572;
Bieniek, R. J., *Phys. Rev. A*18 (1978) 392-413.
- [4] Chen, J.C.Y., in: *Advances in Radiation Chemistry VI*, Curtan, M., and Magee, J. L. (eds.) (1968) 245-376.
- [5] Doverspike, L. D., Smith, B. T., and Champion, R. L., *Phys. Rev. A*22 (1980) 393-398.
- [6] Risley, J. A., *Phys. Rev. A*16 (1977) 2346-2351.
- [7] Smith, B. T., Edwards, III, W. R., Doverspike, L. D., and Champion, R. L., *Phys. Rev. A*18 (1978) 945-954.
- [8] Il'in, R. N. Sakharov, V. I., and Serenkov, I. T., *Abstracts of Contributed Papers, XII ICPEAC, Gatlinburg* (1981) 535-536.
- [9] Cheung, J. T., and Datz, S., *J. Chem. Phys.* 73 (1980) 3159-3165.
- [10] Annis, B. K., Datz, S., Champion, R. L., and Doverspike, L. D., *Phys. Rev. Lett.* 45 (1980) 1554-1557.
- [11] Inouye, H., Niurao, K., and Sato, Y., *J. Chem. Phys.* 64 (1976) 1250-1251.
- [12] Fernandez, S. M., Eriksen, F. J., Bray, A. V., and Pollack, E., *Phys. Rev. A*12 (1975) 1252-1260.
- [13] Schulz, G. J., *Rev. Mod. Phys.* 45 (1973) 423-486.
- [14] Cunningham, D. L., and Edwards, A. K., *Phys. Rev. A*8 (1973) 2960-2964.
- [15] Tronc, M., Huetz, A., Landau, M., Pichou, F., and Reinhardt, J., *J. Phys. B Atom. Molec. Phys.* 8 (1975) 1160-1169.
- [16] Fayeton, J., Dhucq, D., and Barat, M., *J. Phys. B: Atom. Molec. Phys.* 11 (1978) 1267-1281. The data used in Fig. 10 was actually obtained with a beam energy of 1000 eV, but our experience has been that such data can be scaled to different energies.
- [17] Darwent, B. de B., *Natl. Stand. Ref. Data, Natl. Bur. Std.* 31 (1970).
- [18] Botschwina, P., Haertner, H., and Sawodny, W., *Chem. Phys. Lett.* 74 (1980) 156-159.
- [19] Amdur, I., Jordan, J. E., Fung, L.W.-M., Hermans, L.J.F., Johnson, S. E., and Hance, R. L., *J. Chem. Phys.* 59 (1973) 5329-5332.
- [20] Nielsen, G. C., Parker, G. A., and Pack, R. T., *J. Chem. Phys.* 66 (1977) 1396-1401.
- [21] Olson, R. E., and Liu, B., *Phys. Rev. A*17 (1978) 1568-1574.

- [22] Krauss, M., Hopper, D. G., Fortune, P. J., Wahl, A. C., and Tiernan, T. O., Potential Energy Surfaces for Air Triatomics, VI. ARL TR 75-0202, Aerospace Res. Laboratories (1975).
- [23] Tuan, V. N., and Esaulov, V. A., Abstracts of Contributed Papers, XII ICPEAC, Gatlinburg (1981) 531-532.