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Dissociative attachment in HCl, DCl, and F₂

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Resonant scattering models, using nonlocal decay widths, are developed for dissociative attachment of slow electrons to diatomic molecules. Cross sections are obtained for HCl and DCl in several initial rotational and vibrational states, and the dependence of the average attachment cross section upon the rotational and vibrational temperature is examined. For F₂ the cross section for ground state molecules agrees well with experiment above 0.2 eV but shows no zero energy peak. The attachment cross section is higher for vibrationally excited molecules, but the enhancement is much less than that found in H₂ and HCl.

I. INTRODUCTION

It has been shown both experimentally¹ and theoretically² that the cross sections for the attachment of slow electrons with H₂ and D₂ are increased by several orders of magnitude if the molecules are vibrationally excited. This leads to a strong dependence of the attachment rate upon the neutral temperature in ionized gases. Recent experiments³ on HCl and DCl have shown that the rate of dissociative attachment for slow electrons is enhanced dramatically when the temperature is raised from 300 to 1200 K. Although the energy dependence of the cross section suggested that the effect cannot be attributed solely to vibrational excitation within the target molecules, Allan and Wong³ concluded that the value of the attachment cross section near threshold is increased by factors of ~40 and 900 due to excitation to the $v = 1$ and $v = 2$ levels, respectively.

The inverse process of associative detachment



has been studied by Zwier *et al.*⁴ From measurements of the intensity of the infrared radiation emitted by the HCl molecules, they deduce that the relative probability for formation of the $v = 1$ and $v = 2$ levels is 5:3. One of the aims of this work is to study the consistency of these two experiments.

These experiments only provide indirect evidence concerning the cross sections for attachment of electrons to HCl molecules in specific vibrational states. Such information is needed for a better understanding of negative ion formation in XeCl lasers and for the development of gaseous dielectrics. A second goal of this work is to provide a set of cross sections that are consistent with the data of Allan and Wong.³

Dissociative attachment of electrons to F₂ has been studied by many authors. The cross section has been measured in a beam experiment by Chanry.⁵ He finds a cross section that decreases monotonically from $4 \times 10^{-15} \text{ cm}^2$, at a nominal energy of 0 eV, to $3.55 \times 10^{-19} \text{ cm}^2$ at 4.2 eV. The most interesting aspect of these results is the very narrow peak near zero energy. At 0.1 eV, the cross section is only $6.5 \times 10^{-16} \text{ cm}^2$. A similar low energy peak is seen in the semiempirical

calculations of Hall,⁶ but is not found in the *ab initio* calculations by Hazi *et al.*⁷ Hall's result seems to be inconsistent with the Wigner threshold laws and so deserves reconsideration.

Dissociative attachment is usually regarded theoretically as a resonant scattering process, involving the formation and dissociation of a molecular negative ion, e.g.,



The theory often makes full use of the Born-Oppenheimer approximation, by assuming that the capture or emission of the electron can be accomplished without any instantaneous change in the position or velocity of the nuclei. We can then associate a complex potential curve with the negative ion state, the real part specifying the electronic energy and the imaginary part $\Gamma(R)$ giving the lifetime against autodetachment. This is called the local-width approach. Unfortunately, this approach is inconsistent with the conservation of total energy. Since the energy remaining in the residual molecule HCl or F₂ after an electron is emitted is quantized, the energy available to the escaping electron is limited by the motion of the nuclei. Thus, we cannot determine the rate of autodetachment accurately without considering how easily the nuclear vibrational motion can return to one of the allowed eigenstates. This problem may not be serious if the energy available to the detaching electron is large compared to the vibrational spacing, but it must be taken into account for collisions of low energy electrons. We will do this by using a theory with a nonlocal width.

The application of resonant scattering theory requires the existence of discrete states of the negative ion, so that potential curves can be defined. This seems reasonable whenever a mechanism can be identified that will hinder the escape of the extra electron, and so support a quasibound state. The most common mechanism is a centrifugal barrier, which arises when the spatial symmetry of the negative ion state differs from that of the neutral. This pertains to F₂ where the F₂⁻ ground state has symmetry $^2\Sigma_u^-$, whereas the F₂ ground state

is $^1\Sigma_g$. Autodetachment from F₂⁻ is then hindered by a *p*-wave barrier. On the other hand, both the HCl and HCl⁻ states have Σ symmetry and emission of an *s*-wave electron is possible from HCl⁻. This casts doubt on the validity of the resonant scattering model.

Ab initio calculations on HCl⁻ are inconclusive. Goldstein *et al.*⁸ and Krauss and Stevens⁹ were able to locate discrete states embedded in the electron scattering continuum, but they disagree concerning the potential curves. Also the degree of stability of each of these eigenvalues is unclear. The observed cross sections for vibrational excitation in *e*-HCl collisions¹⁰ show broad peaks around 3 eV that could be consistent with a short-lived HCl⁻ resonance with a potential curve similar to that obtained by Krauss and Stevens.

An alternative picture of the formation and decay of HCl⁻ has been suggested by Gauyacq and Herzenberg.^{11,12} In their approach, which employs the zero-range-potential model,¹³ the capture and emission of electrons is regarded in terms of the breakdown of the Born-Oppenheimer separation. We hope that a comparison of our predictions with their results will test the relative merits of the two approaches.

II. THEORETICAL METHOD

The basis of our approach is to split the wave function $\Psi(q, R)$ representing electron scattering by the molecule *XY* into two parts that we will call $\Psi_P(q, R)$ and $\Psi_Q(q, R)$. The symbol *q* is used to denote the coordinates of all of the electrons, and *R* is the nuclear separation. The portion $\Psi_P(q, R)$ describes the long-range interactions between the extra electron and the molecule, whereas $\Psi_Q(q, R)$ is dominant in the strong interaction region where all electrons are close to at least one of the nuclei. The dissociative attachment channel *X* + *Y*⁻ will be described within Ψ_Q , since the extra electron is retained by one of the nuclei.

Applying the Born-Oppenheimer separation to Ψ_Q , we write

$$\Psi_Q(q, R) = \phi_d(q, R)\zeta_d(R). \quad (3)$$

Let us assume that the electronic wave function $\phi_d(q, R)$ is insensitive to the energy of the incident electron. It might correspond to the eigenfunction obtained in a stabilization calculation¹⁴⁻¹⁶ in which the electronic Hamiltonian is diagonalized in a subspace defined by orbitals with sizes not greatly exceeding those of the electrons in the target molecule. The expectation value of the electronic energy

$$\langle \phi_d(q, R) | H_{e1} | \phi_d(q, R) \rangle = E_d(R) \quad (4)$$

then represents the potential curve obtained in such a stabilization calculation.

The wave function $\zeta_d(R)$ which describes the motion of the nuclei, as modified by the proximity of the extra electron, must be determined for all *R*, including the asymptotic region. Since the kinetic energy of the separating nuclei is small, we cannot neglect the dependence of $\zeta_d(R)$ on the energy of the incident electron.

Following Fano¹⁷ and Bardsley,^{18,19} we expand the remaining portion $\Psi_P(q, R)$:

$$\Psi_P(q, R) = \sum_v \int dE' b_v(E') \psi_{vE'}(q, R) \chi_v(R) \quad (5)$$

in which the $\chi_v(R)$ represent the nuclear vibration states in the neutral molecule and the $\psi_{vE'}(q, R)$ describe the elastic scattering of electrons by molecules in specific vibrational states. The coupling between the two parts is controlled by the matrix elements

$$V_{vE}(R) = \langle \psi_{vE}(q, R) | H_{e1} - E | \phi_d(q, R) \rangle. \quad (6)$$

Combining the two portions of the wave function, we obtain

$$\Psi(q, R) = \sum_v \int dE' b_v(E') \psi_{vE'}(q, R) \chi_v(R) + \phi_d(q, R)\zeta_d(R). \quad (7)$$

The unknown coefficients $b_v(E')$ and $\zeta_d(R)$ can be found by diagonalization of the complete Hamiltonian and the imposition of the appropriate boundary conditions. If the initial vibrational state is $\chi_{v_i}(R)$, then $\Psi_P(q, R)$ can contain incoming waves only in the term with $v = v_i$. We then find¹⁹

$$b_v(E') = \delta_{vv_i} \delta(E - E') + \left[\frac{1}{E - E'} - \pi i \delta(E - E') \right] \times \int dR \chi_v^*(R) V_{vE}(R) \zeta_d(R) \quad (8)$$

and

$$\left[-\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + E_d(R) - E \right] \zeta_d(R) = - \sum_v V_{vE}(R) \chi_v(R) \times \left[\delta_{vv_i} - i\pi \int dR' \chi_v^*(R') V_{vE}^*(R') \zeta_d(R') \right]. \quad (9)$$

In the derivation of Eq. (9), we have neglected the energy shift arising from the principal part of the integral over $b_v(E')$. Since we plan to determine $E_d(R)$ empirically, we could assume that this energy shift has been incorporated in $E_d(R)$. However, this assumption would be inappropriate if the energy shift were strongly energy dependent, as has been suggested by Domcke and Cederbaum.²⁰

The two terms on the right-hand side of Eq. (9) have simple physical interpretations. The first describes the formation of the temporary negative ion and so depends only on the initial nuclear wave function $\chi_{v_i}(R)$ and the corresponding electronic coupling element $V_{vE}(R)$. The second term describes the decay of the negative ion through autodetachment and contains a contribution from each open channel. If many channels are open and the matrix elements $V_{vE}(R)$ depend only weakly on *v*, then this sum over vibrational states can be calculated approximately using the closure relation

$$\sum_v \chi_v(R) \chi_v^*(R') \approx \delta(R - R'). \quad (10)$$

The decay term then is proportional to $\zeta_d(R)$ and has the form assumed in the local potential theory. However, this approximation should not be used when there are only a small number of open channels, or if the matrix

elements $V_{vE}(R)$ are very sensitive to the energy of the emitted electron. In the applications considered in this paper this approximation would be inappropriate.

Equation (9) can be solved noniteratively through the introduction of the Green function for the corresponding homogeneous solution, using techniques developed for the study of dissociative recombination.^{18,22} The cross section for dissociative attachment is then obtained by comparing the flux of outgoing ions with that of incident electrons. This gives

$$\sigma_{DA}(E) = \frac{\pi^2}{k_i^2} g \frac{K}{M} \lim_{R \rightarrow \infty} |\zeta_d(R)|^2, \quad (11)$$

in which K and M are the wave number and reduced mass associated with the dissociation fragments in the center-of-mass frame, g is the ratio of the statistical weights of the intermediate negative ion state and the target electronic state, and k_i is the wave number of the incident electron.

III. APPLICATION TO F₂

Our major goal is to see how well the experimental data on dissociative attachment⁵ is fitted by the contribution from a single resonant state. The potential curves for the ground states of F₂ and F₂⁻ have been calculated by Rescigno and Bender.²² Their calculations suggest that the two curves cross very close to the equilibrium separation in the neutral molecule. Since this behavior should lead to attachment cross sections that peak close to zero, their curve for F₂⁻ was used as the starting point for our studies. For both potentials we used Morse representations

$$V(R) - V(R_e) = D(1 - \exp[-\beta(R - R_e)])^2. \quad (12)$$

The parameters for the neutral state, $D^0 = 0.059$, $R_e^0 = 2.66$, $\beta^0 = 1.61$ (all in a.u.), were based on experimental data. For the negative ion state the values $D^- = 0.047$ and $R_e^- = 3.70$ were taken from the calculations of Rescigno and Bender,²² whereas β^- was treated as a variable parameter. The two potentials were connected by imposing the value of 0.125 a.u. upon the af-

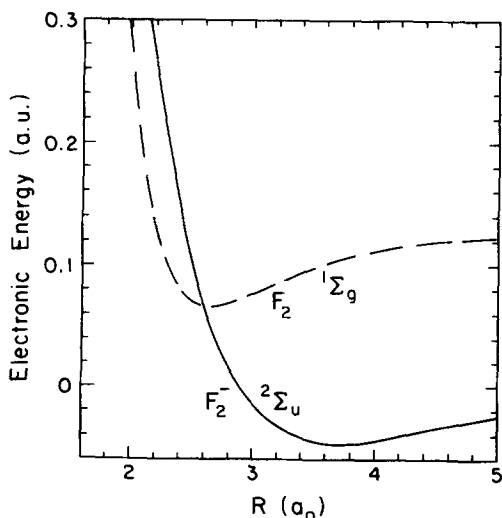


FIG. 1. Potential curves for the ground states of F₂ and F₂⁻.

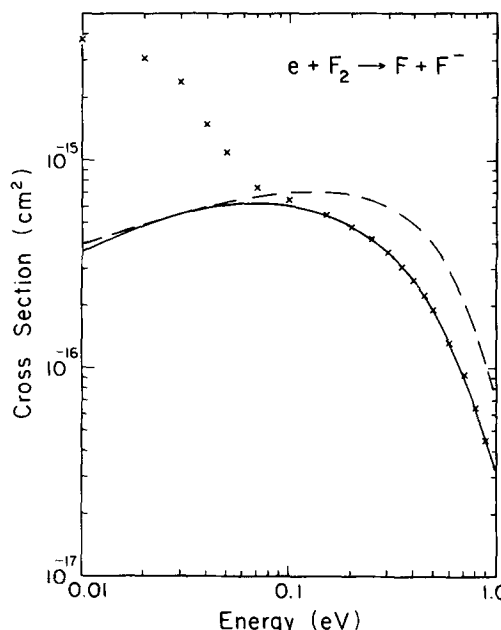


FIG. 2. Cross section for attachment to F₂ molecules in the ground state: x, experimental measurement by Chantry, --- *ab initio* calculation by Hazi, - this work.

finiteness of F⁻.

The matrix element $V_{vE}(R)$ can be appreciated most easily in terms of the equivalent autodetachment width, defined by

$$\Gamma_{vE}(R) = 2\pi |V_{vE}(R)|^2. \quad (13)$$

We will further assume that this width can be written as the product of a barrier penetration factor $f(k_v)$ which determines its energy dependence and an R -dependent factor, which is independent of energy. Thus, we write

$$\Gamma = f(k_v)\gamma(R) \quad (14)$$

with

$$f(k) = \frac{2\rho^3 k^3}{1 + \rho^2 k^2} \quad (15)$$

and

$$\gamma(R) = \begin{cases} \gamma^0, & \text{for } R < R_v \\ \gamma^0 \exp(-\alpha(R - R_v)^2), & \text{for } R > R_v. \end{cases} \quad (16)$$

Here, k_v is the wave number of the emitted electron when the molecule is left in the vibrational state v . In the barrier penetration factor, ρ is a measure of the range of the short-range interactions.

The parameters α and R_v were set to 1.0 and 3.0, respectively, so that the width is constant near $R = R_e^0$ and falls monotonically at larger R . The remaining parameters, γ^0 and ρ , were varied to fit the experimental data.⁵ The best fit was obtained with $\beta^- = 0.853$, $\gamma^0 = 0.0013$, and $\rho = 10$. As shown in Fig. 1, the ground state potential curves cross at $R = 2.60$, which is less than the equilibrium separation in F₂, but well within the Franck-Condon region in the ground vibrational state.

As can be seen from Fig. 2, we were able to fit the

experimental cross sections very well for energies between 0.15 and 1 eV. However, below 0.1 eV, the experimental results are significantly higher than ours. The difficulty in obtaining a better fit arises from the threshold behavior of the calculated cross sections. Since the resonance has odd parity the lowest contributing partial wave has $l = 1$. The reaction is exothermic and there is no Coulomb interaction between the colliding particles. The resonant cross section must then be proportional to $E^{0.5}$ near threshold and must vanish at zero energy. The theory of Hall⁶ did not have this threshold behavior, due to his choice of local-width formalism.

There clearly must be some contribution to dissociative attachment arising from the capture of s -wave electrons. In the limit of zero energy, this s -wave contribution must dominate, since it will be proportional to $E^{-0.5}$. However, the resonance model suggests that the constant of proportionality is small. This is because the symmetries of the lowest electronic state of F₂ are $^2\Sigma_u$, $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_g$. Thus, the first negative ion state that can be formed through the capture of an s -wave electron is the fourth state ($^2\Sigma_g$). The probability that this state is formed in a collision of an electron with energy below 0.1 eV would seem to be very small. Further theoretical and experimental study of the zero-energy behavior would be worthwhile.

An independent check of the low energy cross sections is provided by measurement of the thermal attachment rate. Sides, Tiernan, and Hanrahan²³ find the rate constant to be $(3.1 \pm 1.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at a temperature of $\sim 350 \text{ K}$ and $(4.6 \pm 1.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ near 600 K. The rates computed from our cross sections are 7×10^{-9} and $9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively. Thus, although the temperature dependence is similar, the measured values are below the calculated ones, in contrast to the situation shown in Fig. 2, where the experimental cross sections exceed the theoretical values.

Hazi, Orel, and Rescigno⁷ have used a similar formalism to that described here, but they have computed the coupling matrix elements $V_{v,E}(R)$ using the Stieltjes moment theory. Their results differ from

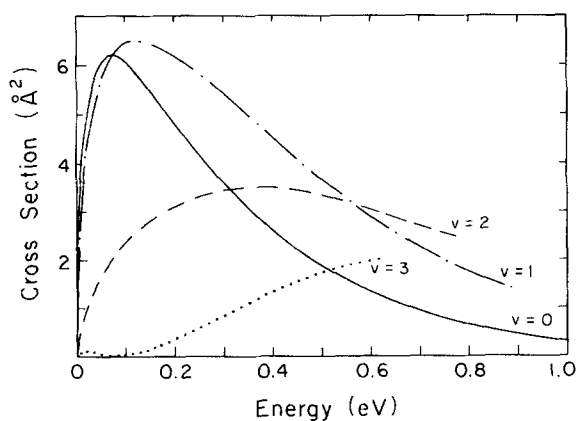


FIG. 3. Calculated cross sections for attachment to F₂ in various vibrational states: — $v = 0$; - - - $v = 1$; - · - $v = 2$; · · · $v = 3$.

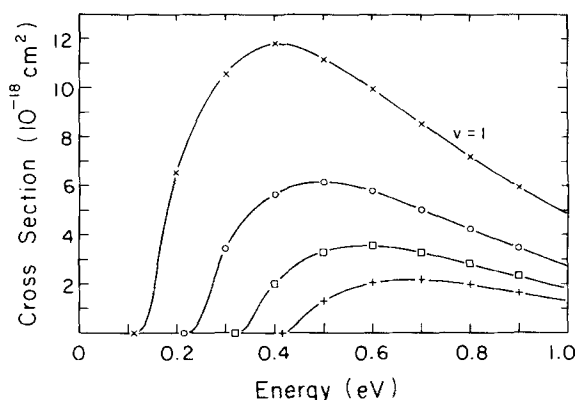


FIG. 4. Calculated cross sections for vibrational excitation to various levels: -×- $v = 1$; -○- $v = 2$; -□- $v = 3$; -+- $v = 4$.

ours by at most a factor of 2, and show the same threshold behavior. The agreement is excellent in view of the difficulty of performing *ab initio* calculations on this system.

In Fig. 3, we show the cross section for attachment to molecules in various vibrational states. The results are qualitatively similar to those obtained by Hazi *et al.*⁷ and the peak values of each cross section differ by at most 20%. A qualitative check of these results is provided by Trainor and Jacob's²⁴ study of attachment in an electron-beam-controlled gas discharge. Working with an electric field that produces an average electron energy of around 1 eV, they find that increasing the gas temperature from 300 to 500 K results in an increase in the attachment rate of almost 25%. In this energy range, the ratio of the attachment cross sections for $v = 0, 1,$ and 2 is approximately 1:4:6, which would lead to an enhancement in the attachment rate of 26% due to this change in temperature.

We have noted above that Hall's local resonance model and our nonlocal theory give the same attachment cross sections at energies above 0.2 eV. However, the resonance parameters are very different and other predictions of the models are different. In Fig. 4, we show the vibrational excitation cross sections computed using this theory. The cross sections are much smaller than that obtained by Hall,⁶ by almost one order of magnitude, but the shapes and cross section ratios are very similar. However, the contributions are so small that the $^2\Sigma_u$ resonance may not dominate the cross sections for excitation of the low-lying vibrational levels. Experimental determinations of these cross sections would be very helpful in assessing the merits of these two resonance models.

IV. APPLICATION TO HCl AND DCI

As stated in the Introduction, the application of resonant scattering theory to e -HCl scattering is controversial. In view of the success of calculations on attachment using this approach by Abouaf and Fiquet-Fayard,^{25,26} it seems worthwhile to test the theory against the experimental results of Allan and Wong³ on the temperature dependence of dissociative attachment,

and Zwier *et al.*⁴ on the reverse reaction of associative detachment. The results can then be compared with those obtained by the zero-range-potential method.^{11-13,27,28}

The essential assumptions of the theory are that for scattering of electrons by HCl molecules with internuclear distance in the range 2.5 to 2.9 a_0 , the shape of the electronic wave function in the neighborhood of the nuclei is relatively insensitive to the energy and so is dominated by the energy-independent term $\phi_d(q, R)$ introduced in Eq. (3), and that the matrix elements defined in Eqs. (4) and (6) can be parametrized simply. The choice of the diagonal matrix element $E_d(R)$ will be guided by the *ab initio* calculations of Krauss and Stevens,⁹ who constrained their electronic orbitals to remain tight as the internuclear distance was reduced below the value at which HCl⁻ becomes unstable against electron emission.

For the neutral HCl molecule the Morse potential was modified to allow for the ionic character at moderately large R . Fitting to the low-lying vibrational levels, we took

$$V^0(R) = 0.5 - \frac{1}{R} (1 + 1.839 \exp[-\beta^0(R - R_e^0)] - 1.546 \exp[-2\beta^0(R - R_e^0)]) \quad (17)$$

with $\beta^0 = 0.4288$ and $R_e^0 = 2.409$. For the negative ion curve, we added an adjustable exponential term to a Morse potential whose parameters were chosen on the basis of the *ab initio* calculations.⁹ The best fit was obtained using

$$E_d(R) = D^- \{ \exp[-2\beta^-(R - R_e^-)] - 2 \exp[-\beta^-(R - R_e^-)] \} + A \exp(-aR) \quad (18)$$

with $D^- = 0.0135$, $R_e^- = 3.6$, $\beta^- = 0.7$, $A = 250$, and $a = 4.0$. The threshold for dissociative attachment was assumed to be 0.2995 a.u. (0.815 eV). These potential curves, drawn in Fig. 5, lead to an apparent stabiliza-

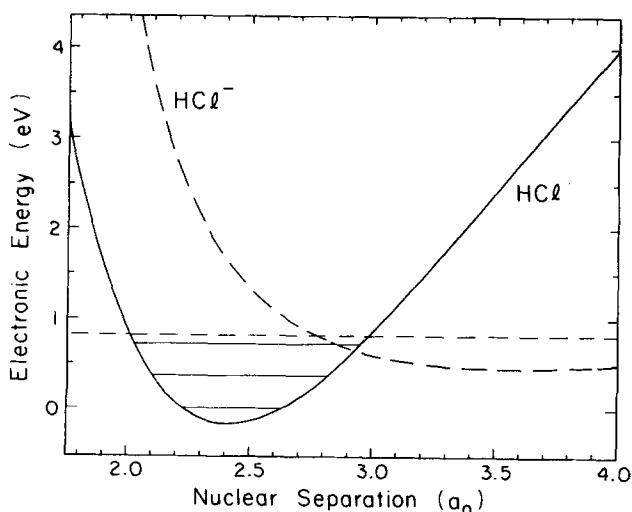


FIG. 5. Potential curves for the ground states of HCl and HCl⁻. For $R < 2.92$, the negative ion curve corresponds to the results of a stabilization calculation.

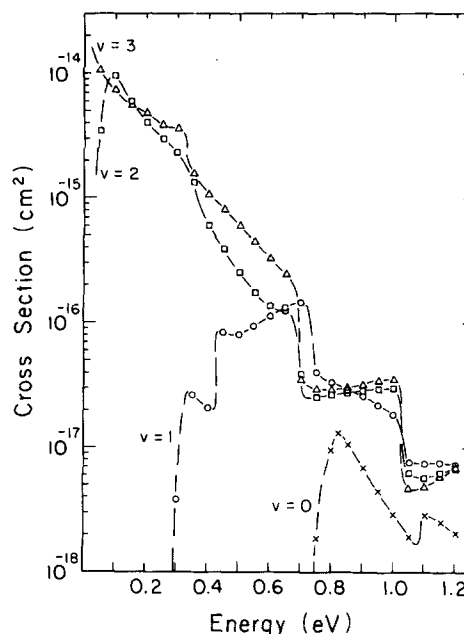


FIG. 6. Cross sections for attachment to HCl in specific vibrational states, averaged over a thermal distribution of rotational states: \times — $v=0$; $-O-$ $v=1$; $-O-$ $v=2$; $-\Delta-$ $v=3$.

tion point at 2.92 a_0 , near the edge of the Franck-Condon region for the $v=2$ level of the neutral molecule. The zero-range potential analysis of Dube and Herzberg suggests that the stabilization point for the adiabatic negative ion curve is near 2.5 a_0 .

Once again we assume that the autodetachment rate is given by Eqs. (14) and (16) with $f(k) = k^{0.33}$, $\gamma_0 = 0.33$, and $R = 3.0$. In choosing the exponent in $f(k)$, we have taken into account the long range dipole interaction. The form specified in Eq. (15) is suitable only for p -wave resonances as in F₂.

A. Dissociative attachment to HCl

With these parameters, we have computed the cross sections for attachment to HCl molecules in vibrational states $v=0-3$ and rotational states $J=0-25$, for electron energies between 0.05 and 1.20 eV, at intervals of 0.05 eV. In many applications, the rotational states of the molecules will be in thermal equilibrium. Hence, we have averaged our cross sections over a thermal distribution of rotational states, for temperatures between 300 and 1200 K. Tables of these values are available from the authors. In Fig. 6, we show the results at room temperature.

The cross section for the ground vibrational state is lower than that for excited states at all energies, due to the relatively large value of the stabilization distance. However, the major enhancement in the attachment rate for vibrationally excited molecules comes from the lowering of the threshold, and so is most apparent at low electron energies.

To compare with the measurements by Allan and Wong,³ we must make a further average over a Boltz-

mann distribution of vibrational states. Figure 7(a) shows the results for a temperature of 1000 K. The calculated cross sections are absolute, but the experimental values are relative, and so are normalized to the calculations near 0.8 eV. The parameters in the resonance model have been chosen to give agreement in the cross sections at the three peaks at lower energies. The agreement between theory and experiment would be improved, particularly at energies above 0.8 eV, if allowance were made for the finite resolution of the experiment. However, there appears to be a significant difference, of about 0.1 eV, in the position of two of the structures.

The peak marked *a* in Fig. 7(a) is close to the threshold for ground state molecules and is the only one which appears in this energy range at low temperatures. Peak *b* arises from attachment to molecules in the ground vibrational states with $J \geq 10$. Peak *c* is caused by molecules with $v = 1$ and $J \geq 10$, and peak *d* by molecules in states with $v \geq 2$. Note that there is no peak near the threshold for attachment to molecules with $v = 1$ and $J = 0$ (at 0.45 eV). Further insight into the formation of this structure can be obtained from Fig. 8, where we show the cross sections at a fixed energy excess above the threshold for each value of v and J . Note that for $J \geq 9$ attachment to molecules with $v = 2$ becomes exothermic. Thus, for attachment to molecules with $v = 0$ or 1 and $J \geq 9$ there is a range of energies for which dissociative attachment is allowed, but excitation of the $v = 2$ level is not. The reduction of the attachment

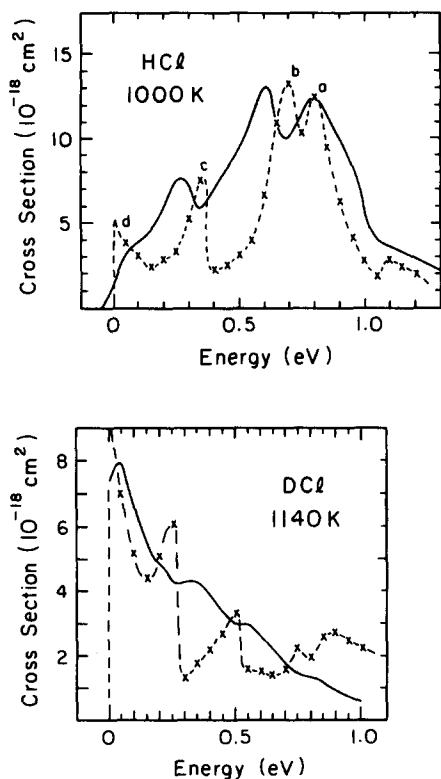


FIG. 7. Attachment cross sections for a gas at high temperature: (a) HCl at 1000 K; (b) DCI at 1140 K: --- measurements of Allan and Wong; -x- this work.

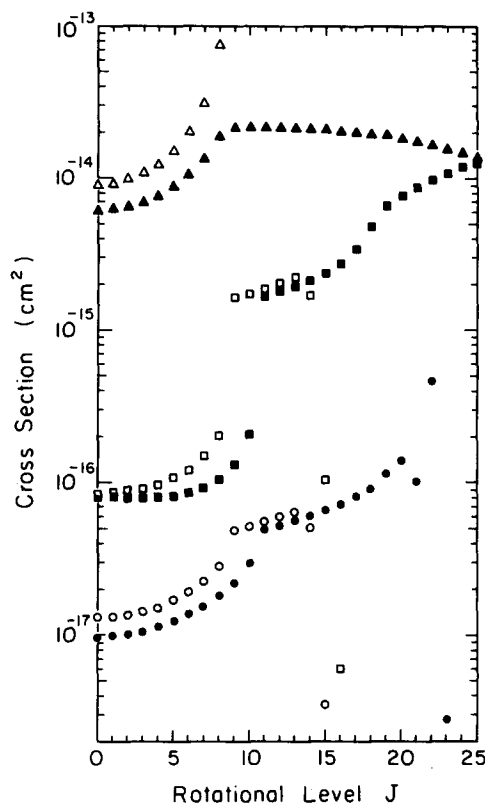


FIG. 8. Calculated threshold cross sections for attachment to HCl in specific states: circles, $v = 0$; squares, $v = 1$; triangles, $v = 2$. The open and closed symbols indicate cross sections at 10 and 50 meV, respectively, above threshold.

cross section due to autodetachment from the HCl⁻ ion is then reduced and the cross section is thus enhanced. This can be seen especially clearly for $v = 1$ in Fig. 8. For $J \leq 9$, the threshold values of $\sigma_{v=1}^{PA}$ appear to be anomalously low, due to a cancellation in a vibrational overlap matrix element. The fit with experiment seen in Fig. 7(a) would be improved if these values were raised significantly, as suggested below.

For scattering by ground state molecules the attachment cross section peaks just above $1.3 \times 10^{-17} \text{ cm}^2 \sim 10 \text{ meV}$ above threshold. This value is intermediate between the experimental values of $8.9 \times 10^{-18} \text{ cm}^2$ reported by Azria *et al.*²⁹ and $2.0 \times 10^{-17} \text{ cm}^2$ obtained by Compton *et al.*³⁰ Chantry³¹ has suggested that the results of Azria *et al.*²⁹ should be raised slightly. Analyses³² of recent swarm experiments³³ support the larger value for the maximum cross section.

B. Attachment to DCI

Two further checks on the theory can be performed by applying the model to $e + \text{DCI}$ collisions. For ground state molecules the peak value of the cross section was measured by Azria *et al.*²⁹ to be about 20% of that for HCl. Our calculation leads to a peak value of almost $3 \times 10^{-18} \text{ cm}^2$, which is 23% of the HCl peak value. Comparison with the high temperature measurements of Allan and Wong³ is less successful. The cross section computed for a gas temperature of 1140 K is shown

in Fig. 7(b). Again the experimental result is not absolute. Although the relative enhancement of the low energy peaks in DCl as compared with HCl is well reproduced, the quantitative agreement with experiment is not satisfactory.

C. Associative detachment

The process



leads to molecules in many rotational and vibrational states. These cross sections can be obtained by detailed balance from those for dissociative attachment. Indeed, Fig. 8 contains most of the information needed to evaluate the detachment cross sections for energies of 10 and 50 meV.

Once again, we have two experimental checks of our results. Howard *et al.*³⁴ have measured the total detachment rate coefficient at 296 K to be $9.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, using a flowing afterglow apparatus. Our computed value is $10.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Zwier *et al.*⁴ have measured the relative populations of the vibrational states $v = 1$ and 2 produced in the reaction to be 5:3 at this temperature. From our calculations, the probabilities of forming the levels $v = 0, 1$ and 2 are 4%, 48%, and 48%. Although the agreement is far from perfect, it shows that there is no serious inconsistency between the experiments on the two processes.

Although dissociative attachment and associative detachment are inverse processes, the two experiments do not involve the same molecular states. Thus, in thermal energy, collisions between Cl⁻ and H, rotational quantum numbers up to ~ 20 are important. However, for $e + \text{HCl}$ collisions near room temperature only low values of J are significant (say $J \lesssim 5$). Thus, the measurements of associative detachment rates give us some information on the cross sections of electrons with HCl molecules in high vibrational or rotational states, so we can learn little directly about attachment to states with $v = 0$ and low J .

Gauyacq²⁷ has applied the zero range potential model to associative detachment in F⁻-H and Cl⁻-H collisions. In the latter case, Gauyacq has chosen the potential curve for HCl⁻ to fit the two experiments on associative detachment. From his calculations, performed at an energy of 25 meV, one can derive the cross sections for dissociative attachment near threshold. For HCl molecules with $J = 0$, the values are

$$\sigma_{v=0}^{DA} = 0.6 \text{ \AA}^2 \text{ at } 0.84 \text{ eV}, \quad \sigma_{v=1}^{DA} = 7.9 \text{ \AA}^2 \text{ at } 0.49 \text{ eV},$$

and

$$\sigma_{v=2}^{DA} = 55 \text{ \AA}^2 \text{ at } 0.14 \text{ eV}. \quad (20)$$

The value for the ground state is higher than both experimental measurements^{29,30} and our calculations. That for the state $v = 1$ is much larger than ours, but the value for $v = 2$ is only slightly lower than our value.

V. CONCLUSIONS

Electron attachment to F₂ provides a test of the relative merits of local and nonlocal resonance theories.

However, using the empirical approach the parameters can be chosen to fit the experimental measurements with either theory. Measurements of the vibrational excitation cross sections should help to distinguish between the two theories.

Although we are able to fit the cross sections measured by Chantry between 0.15 and 1 eV through the contributions from the ground $^2\Sigma_u$ state of F₂⁻, we cannot account for the zero energy peak. Further study of this feature would be worthwhile. Because the potential curve for the negative ion crosses that of the neutral molecule close to the equilibrium separation, and the reaction is exothermic, the enhancement of the cross section for attachment to vibrationally excited molecules is only moderate.

The application of resonant scattering theory to attachment to HCl and DCl is only partially successful. We have shown that there is no major inconsistency between the measurements of Allan and Wong,³ which suggest a large value for the ratio of the attachment cross sections $\sigma_{v=1}^{DA}/\sigma_{v=2}^{DA}$, and observation by Zwier *et al.* of almost equal probabilities of formation of $v = 1$ and $v = 2$ states of HCl in associative detachment.⁴ However, the quality of our fit to the experimental data leaves considerable room for improvement. Thus, we eagerly await the results of the calculations of dissociative attachment cross sections using the zero range potential model, which has been applied successfully to vibrational excitation¹³ and associative detachment.²⁷

Padial, Norcross, and Collins³⁵ have recently published close-coupling calculations for scattering of low energy electrons by HCl molecules with the nuclei fixed at the equilibrium distance, taking into account both polarization and exchange interactions. The eigenphase sum shows a rapid rise near 2 eV, but the rise is only through $\pi/3$, and not the full π found in a narrow resonance. This behavior supports the concept of a broad short-lived resonance, but the evidence is not conclusive. At lower energies there is significant scattering due to polarization and exchange effects, as had been observed in HF by Rescigno *et al.*³⁶ Padial *et al.*³⁵ suggest that these effects might depend strongly on R and so could be responsible for the threshold peaks in vibrational excitation. The importance of polarization might explain the limited success of the resonance and zero-range models of dissociative attachment. It should be extremely helpful if Padial *et al.* could repeat their calculations at other values of R .

It should be stressed that these calculations are semiempirical in nature. Small adjustments in one parameter, such as the autoionization width can often be compensated for by changes in another, such as the slope of the negative ion potential curve. Nevertheless, the conclusions of this paper are not sensitive to the particular set of values given above. In this regard, it is perhaps worthy of mention that the potential curves deduced from a semiempirical analysis² of $e\text{-H}_2$ scattering were later confirmed by an *ab initio* calculation.³⁷

Although we are unable to improve the fit to experiment by varying the parameters in the resonance model,

we can identify changes in the threshold cross sections, shown in Fig. 8, that would accomplish this. The cross sections $\sigma_{v=0}^{DA}$ should be raised by about 25%; $\sigma_{v=1}^{DA}$ should be increased by a factor of ~ 5 for $J \leq 9$ and by $\sim 25\%$ for $J \geq 10$, and $\sigma_{v=2}^{DA}$ should be reduced by about 25%. Thus, for attachment to ground state molecules, we recommend a peak value just below $2 \times 10^{-17} \text{ cm}^2$.

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