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Ab Initio Study of Dissociative Attachment of Low-Energy Electrons to F_2

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Adiabatic-nuclei resonance theory has been applied to the study of dissociative attachment of low-energy electrons to F_2. Stieltjes moment theory was used to derive fixed-nuclei electronic resonance parameters from large-scale configuration-interaction calculations on F_2 and F_2^-. Dissociative attachment cross sections for the four lowest vibrational levels of F_2 are reported and compared with available experimental data.

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Recent interest in rare-gas fluoride molecules in *e*-beam and discharge-excited laser devices has prompted a large number of experimental investigations[1-7] of electron attachment in low-energy $e^- + F_2$ collisions. A knowledge of the energy dependence of the cross section for the process

$$e^- + F_2 \rightarrow F + F^- \tag{1}$$

is important for the kinetic modeling of these lasers. There is also much current interest in the dependence of the attachment rate on the vibrational temperature of F_2, since recent experiments[8] have reported a substantial improvement in fluorescence efficiency with heated gas mixtures.

There have been three previous theoretical studies of dissociative attachment in F_2,[9-11] all semiempirical treatments employing parameters determined by a best fit to a portion of experimental attachment data. Drukarev and Pozdneev[10] used the Faddeev equations to calculate the cross section with a simple, separable potential describing the electron-fluorine interaction.

Hall[9] employed the so-called "boomerang" or complex-potential model[12,13] to describe the motion of the nuclei, and to calculate both dissociative attachment and vibrational excitation cross sections for F_2. However, the assumptions underlying this model are questionable[14-16] at the very low ($\lesssim 1.5$ eV) energies where the $^2\Sigma_u{}^+$ resonance of $F_2{}^-$ dominates the scattering, and the calculated cross sections[9] did not have the correct behavior at the thresholds. In very recent work, Bardsley, Derkits, and Wadehra[11] used a more rigorous treatment of nuclear motion[14] and explicitly took into account the energy dependence of the resonance width to avoid this difficulty.

Because a considerable amount of experimental data is available for electron attachment to F_2, and because, to our knowledge, there have been no previous *ab initio* calculations of dissociative attachment for *any* molecule, we have undertaken an extensive theoretical study of low-energy, electron-F_2 collisions. Here, we report dissociative-attachment cross sections for the four lowest vibrational states of F_2 at electron energies from 0 to 1 eV. The present work is novel for several reasons. It is the first theoretical study of dissociative electron attachment which treats both the electronic and the nuclear motions *ab initio*, and which uses no experimental cross sections as input. We employ rigorous resonance scattering theory,[17] formulated within the Born-Oppenheimer or adiabatic nuclei approximation, to describe the dynamics of the nuclei, and make only two additional assumptions to simplify the theory. The required electronic resonance parameters are extracted from large, multiconfiguration wave functions for $F_2(^1\Sigma_g{}^+)$ and $F_2{}^-(^2\Sigma_u{}^+)$ which include both target-polarization and electron-correlation effects.

The wave equation governing the motion of the dissociating nuclei $(F+F^-)$ at total energy E is

$$[-(1/2\mu)(d^2/dR^2)+V(R)+W_E(R)-E]\varphi_{Ev_i}(R) = -U_{v_i}(E-\epsilon_{v_i},R), \qquad (2)$$

where φ_{Ev_i} is the nuclear wave function associated with the electronic resonance state, $V(R)$ is the "unshifted" potential-energy curve of the negative ion, and $U_v(\epsilon,R)$ is the matrix element coupling the resonance to the nonresonant scattering solution associated with a vibrational level v. $U_v(\epsilon,R)$ is defined as

$$U_v(\epsilon,R)=[\Gamma(\epsilon,R)/2\pi]^{1/2}X_v(R), \qquad (3)$$

where $\Gamma(\epsilon,R)$ is electronic resonance width and we assume $U_v(\epsilon,R)$ to be real. $W_E(R)$ is a complex, energy-dependent, nonlocal potential defined by

$$W_E(R)\varphi_E(R)=\sum_v \mathrm{P}\int_0^\infty \frac{d\epsilon U_v(\epsilon,R)\int dR' U_v{}^*(\epsilon,R')\varphi_E(R')}{E-\epsilon-\epsilon_v} - i\pi\sum_v^{\text{open}} U_v(E-\epsilon_v,R)\int dR' U_v{}^*(E-\epsilon_v,R')\varphi_E(R'), \qquad (4)$$

where $E=\frac{1}{2}k_v{}^2+\epsilon_v$ and $\frac{1}{2}k_v{}^2$ is the (asymptotic) kinetic energy of the electron. ϵ_v and X_v denote the energy and wave function, respectively, of the vth vibrational level of the neutral target molecule, F_2. Note that the second sum on the right-hand side of Eq. (4) is restricted to the energetically open channels.

For dissociative attachment, a regular solution to Eq. (2) is constructed subject to purely outgoing boundary conditions. The integrated cross section for dissociative attachment starting in level v_i is then given as

$$\sigma_{v_i\to \mathrm{DA}}=(2\pi^2/k_{v_i}{}^2)(K/\mu)\lim_{R\to\infty}|\varphi_{Ev_i}(R)|^2, \qquad (5)$$

where $K^2/2\mu$ is the asymptotic kinetic energy of the dissociated fragments with reduced mass μ. In order to make the numerical solution of Eq. (2) tractable, the principal-value integral in Eq. (4) was simplified by replacing ϵ_v in the denominator by an average value $\bar{\epsilon}$ and summing the vibrational levels to yield

$$\sum_v \mathrm{P}\int d\epsilon \approx (2\pi)^{-1}\mathrm{P}\int d\epsilon \frac{\Gamma(\epsilon,R)\varphi_E(R)}{E-\epsilon-\bar{\epsilon}}. \qquad (6)$$

In order to solve Eq. (2), one needs the potential-energy curves of both F_2 and $F_2{}^-$, as well as the resonance width $\Gamma(\epsilon,R)$. We used the method of configuration interaction (CI)[18] to calculate these electronic parameters for fourteen internuclear distances between $2.4a_0$ and $100a_0$. Here we summarize only the most important points, and will present the details of the calculation elsewhere.[19] The $^1\Sigma_g{}^+$ ground electronic state of F_2 was represented by a 24 configuration wave function constructed from "natural" molecular orbitals,[18] which, in turn, were determined from a so-called "first-order CI" treatment with use of two reference configurations.[18] The orbital basis consisted of $9\sigma_g$, $7\sigma_u$, $5\pi_g$, $5\pi_u$, $1\delta_g$, and $1\delta_u$ functions. The resonant part of the $F_2{}^-(^2\Sigma_u{}^+)$ state was represented by a first-order CI wave function with 182 configurations constructed from the same orbital basis. The nonresonant background was described by all possible, antisymmetrized, Kronecker products of the 24 F_2 configurations and ten diffuse σ_u molecular orbitals which were added to the original basis to represent the scattered electron. The total CI space was 501 configurations.

Our calculated dissociation energies of $F_2(^1\Sigma_g{}^+)$ and $F_2^-(^2\Sigma_u{}^+)$ are 1.77 and 1.19 eV, respectively, and compare favorably with the experimental values of 1.68 and 1.29 eV. Our wave functions, however, underestimate the electron affinity of atomic fluorine by 0.4 eV (2.99 eV calculated vs 3.40 eV experimental). Since very large CI wave functions would be required to obtain an accurate value for this quantity, we have chosen to shift our calculated potential curve of F_2^- by 0.4 eV to obtain the correct asymptotic limit at infinite internuclear separation. With this adjustment, $F_2^-(^2\Sigma_u{}^+)$ becomes autodetaching for $R \leqslant 2.63a_0$, whereas the calculated equilibrium internuclear distance of $F_2(^1\Sigma_g{}^+)$ is $2.68a_0$.

The resonance width was calculated from the above-mentioned wave functions with use of the Stieltjes moment-theory technique.[20] The ten diffuse σ_u orbitals were chosen to obtain a good representation of the background continuum for electron energies between 0 and 4 eV. For a fixed energy, the calculated width increases rapidly as the internuclear distance decreases from $2.63a_0$, while, for a fixed value of R, the width reaches its maximum near 1 eV. Some typical peak values are $\Gamma = 0.22$ eV at $R = 2.59a_0$, $\Gamma = 0.48$ eV at $R = 2.50a_0$, and $\Gamma = 1.43$ eV at $R = 2.35a_0$.

Figure 1 shows the dissociative-attachment cross sections which we have calculated for the four lowest vibrational states of F_2 using ϵ_0 for $\bar{\epsilon}$ in Eq. (6). The ground-state cross section rises steeply from threshold, reaching a peak value of 7.1 Å^2 at 0.16 eV. With increasing initial vibrational excitation, the peak moves to higher electron energies, while the maximum value of the cross section increases from $v = 0$ to $v = 1$ but decreases thereafter. The dependence of the attachment cross section on v is complicated, since it is due to a combination of factors, e.g., the R dependences of X_v, Γ, and φ_E. At an electron energy of 1.0 eV, the effective cross section, averaged over the vibrational population, increases by 10% as T_{vib} increases from 300 to 500 °K, in reasonable accord with experiment.[5] Figure 2 compares the present attachment cross section for the ground vibrational state to previous results. Between 0.15 and 1.5 eV, our cross section is about 1.5–2 times larger than the experimental data of Chantry. In this energy region, the semiempirical calculations[9, 11] manage to reproduce the experimental values closely by appropriate adjustment of the resonance parameters, based on either the measured attachment rate[9] or a part of the cross section.[11] At electron ener-

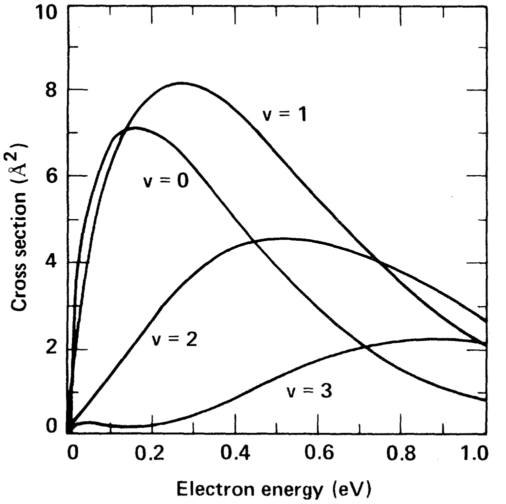

FIG. 1. Calculated dissociative-attachment cross sections $\sigma_{v \to \text{DA}}$ for various vibrational levels of F_2.

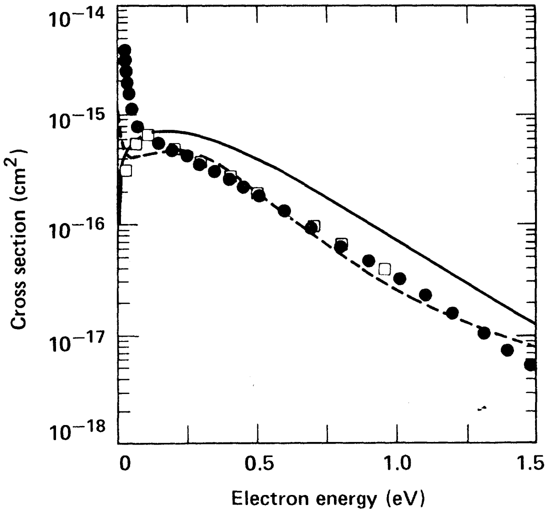

FIG. 2. Comparison of theoretical and experimental dissociative-attachment cross sections for the ground vibrational state of F_2: Solid line, present work; dashed line, Hall (Ref. 9); squares, Bardsley, Derkits, and Wadehra (Ref. 11); solid circles, Chantry (Ref. 7).

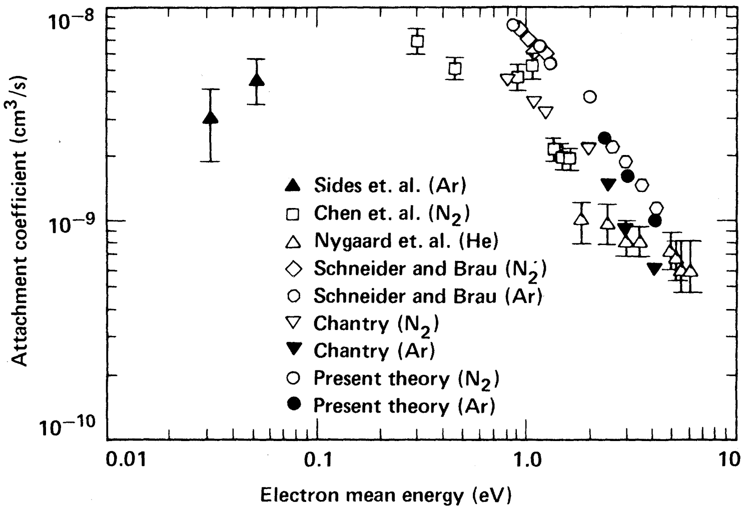

FIG. 3. Comparison of theoretical and experimental dissociative attachment coefficients for F_2. Separate data are shown for different buffer gases, as noted after the authors' names.

gies below 0.15 eV, the theoretical and experimental cross sections differ significantly. In interpreting this region it should be noted that all the calculations, including the present one, treated only the resonant, $^2\Sigma_u$ contribution to dissociative attachment, and that this partial cross section must behave as $E^{1/2}$ at threshold. Both the present cross section and the results of Bardsley, Derkits, and Wadehra[11] show this behavior, and agree well with each other near threshold. The cross section calculated by Hall[9] is quite similar to the experimental data below 0.15 eV; however, it does not satisfy the $E^{1/2}$ threshold law required for the $^2\Sigma_u{}^+$ channel. We have also calculated the dissociative-attachment cross section using our present *ab initio* resonance parameters in the "boomerang" model[9] and obtained results with the same energy dependence as Hall's data.[9] Based on these observations we conclude that the apparent agreement between the "boomerang" model and the experiment near threshold is an artifact due to the breakdown of the assumptions underlying this model at very low electron energies.[14-16, 19] We also believe that no critical comparison between theory and experiment is possible in the 0.0–0.15 eV region, until the nonresonant, $^2\Sigma_g{}^+$ contribution to dissociative attachment is calculated. The $^2\Sigma_g{}^+$ partial cross section diverges as $E^{-1/2}$ at threshold, but this channel is coupled to $F_2^-(^2\Sigma_u{}^+)$ by only small, non–Born-Oppenheimer terms in the Hamiltonian.

Finally, Fig. 3 shows the attachment coefficients calculated with a Boltzmann code from our cross sections for two different gas mixtures (N_2 and Ar), as well as all the available experimental data. The present rate coefficients are in excellent agreement with the data of Schneider and Brau,[4] but they are approximately a factor of 2 higher than the values derived from Chantry's absolute cross sections.[7]

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Novel Analytic Solutions to General Four-Wave-Mixing Problems in a Raman Medium

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A new approach to the problem of steady-state plane-wave propagation in a Raman-active medium has lead to general analytical solutions. Any arbitrary number of fields can interact via both Raman and four-wave processes, but all fields must satisfy the phase-matching condition. The solutions will be illustrated with a problem of current interest; multiple first Stokes generation from a multiple-mode pump field.

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In 1962 Armstrong *et al.*[1] presented the equations governing plane-wave steady-state propagation in a nonlinear medium. They derived explicit analytic solutions for second- and third-harmonic generation when the fields are assumed to satisfy the phase-matching condition, and indicated the procedure to be followed for a higher-order harmonic generation. In 1964 Platonenko and Khokhlov[2] presented analytic solutions to the simplest problem which can exist in a Raman medium, pump conversion to first Stokes. Both these analytic solutions contained the dynamics of the entire process allowing complete depletion of the initial pump fields and saturation of the generated final product fields. Since that time no new analytic solutions have been found which can describe pump depletion and/or saturation. For example, Butylkin *et al.*[3] in 1976 described the generation of the first anti-Stokes field for which it is assumed that there is no back reaction of the anti-Stokes field on the pump-Stokes conversion process. Even with this approximation these solutions are very complicated Gauss hypergeometric functions and indicate the prevailing philosophy that analytic solutions are sufficiently difficult or impossible to obtain and too complex to understand, necessitating the direct use of a computer to generate solutions.[4] In some cases where solutions describing actual experimental conditions are desired a computer may be the only path to a solution. However, in many cases the existence of analytic solutions would allow a valuable qualitative understanding of the physics of a process even if the physics is only absolutely valid for some more simplied model.

In this Letter, I would like to show that a new approach to the original equations derived in 1962 for four-field interactions can lead to simple physically transparent analytic solutions for a very large group of problems when applied to a Raman-active medium. Any arbitrary number of fields can be considered as long as all fields are phase matched and as long as each field has at least one other corresponding field with a frequency chosen to match exactly the two-photon Raman transition, i.e., for example, a problem with a pump, first-Stokes, second-Stokes, etc. or several different pump fields and their corresponding Stokes fields. I will also make some standard approximations and assumptions:

(1) The two-photon Rabi frequency[5] is always sufficiently small such that there is no molecular