that NH₃, HF, HCl, and H₂O₂ should exhibit the same behavior. Table I gives the electric dipole moments of these molecules as well as the critical moment (11). Of course, neither of these molecules produces an electric field identical to the one of an extended dipole. Nevertheless, the fact that the same critical value holds for a point dipole and for a finite dipole, leads one to the conclusion that this critical value is quite insensitive to the higher order multipole components of the electric field, and essentially depends on the dipole moment. A critical value very close to D_0 , as computed here, certainly holds for any type of polar molecule.

It is seen in Table I that H_2S , HCl, and NH_3 have dipole moments below the critical value, whereas the moments of H_2O , D_2O , HF, and H_2O_2 lie above this value.¹⁰ The former molecules thus cannot bind electrons in their dipole fields and electron capture cannot

¹⁰ Mittleman and von Holdt (Ref. 3) in their Fig. 3 attribute a subcritical moment to H₂O. This is due to their omission of a factor 2 when converting from the *D*'s to the dimensionless α 's.

occur for them. This is especially significant for the molecule H_2S , which has been shown to have an anomalous electron scattering cross section.

We are thus led to question seriously the role of electron capture in the scattering of low-energy electrons by polar molecules. At least, this mechanism cannot operate universally, and further investigations clearly are necessary to explain the enhanced cross sections observed for some polar molecules.

Note added in proof. After the present paper was submitted to this journal, the same problem was independently solved by three other groups of workers. M. H. Mittleman and V. P. Myerscough [Phys. Letters 23, 545 (1966)] and J. E. Turner and K. Fox [Phys. Letters 23, 547 (1966)] use rather complicated methods, while W. B. Brown and R. E. Roberts [J. Chem. Phys. (to be published)] use the same method as ours and show that the presence of a repulsive radial core will not modify the value of the critical dipole moment.

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Single- and Double-Quantum Photodetachment of Negative Ions*

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The recent measurement of the transition probability for the double-quantum detachment of an electron from I⁻ has prompted a new theoretical study of this problem. A central-field model for bound and free states is used, in which a parameter is adjusted in the potential to yield the observed binding energies of the negative ions. An implicit-sum method, requiring the solution of inhomogeneous radial equations, is used to evaluate the sums over intermediate states. The results for I⁻ lie almost within the experimental uncertainty. The cross sections for single-quantum photodetachment and electron elastic scattering (from the neutral atom) are also given for the ions studied: C⁻, O⁻, F⁻, Si⁻, S⁻, Cl⁻, Br⁻, I⁻.

I. INTRODUCTION

IN a recent experiment, Hall, Robinson, and Branscomb¹ measured the transition probability (W_2) for the the double-quantum photodetachment of an electron from I⁻ at the ruby-laser wavelength. Their result is higher by a factor of 3 to 6 (considering the experimental uncertainty) than a theoretical estimate made by Geltman.² The latter theoretical estimate was based on the approximation that all the continuum states of the negative ion may be represented by plane waves. This approximation makes trivial the summation over allowed intermediate states (which all lie in the continuum), and yields an expression for W_2 which is simply proportional to σ_1 , the cross section for singlequantum photodetachment. This latter cross section is well known experimentally for I⁻ (Ref. 3), as well as for a number of other negative ions. The present work is an attempt to improve upon the plane-wave approximation by treating one-electron continuum states exacely in an assumed central field.

The interaction Hamiltonian between the radiation field and an atomic electron is

$$H' = -\frac{e}{mc^2} \mathbf{p} \cdot \mathbf{A}(0) + \frac{e^2}{2mc^2} A^2(0) , \qquad (1)$$

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¹ J. L. Hall, E. J. Robinson, and L. M. Branscomb, Phys. Rev. Letters 14, 1013 (1965).

² S. Geltman, Phys. Letters 4, 168 (1963); 19, 616 (1965).

⁸ B. Steiner, M. L. Seman, and L. M. Branscomb, J. Chem. Phys. 37, 1200 (1962).

interaction

where, in taking the vector potential to be a constant in space over atomic dimensions, we are making the dipole approximation. In this approximation, which is always adequate in dealing with radiation in the optical range, all matrix elements of the A^2 term vanish because of the orthogonality of the atomic wave functions. Corinaldesi⁴ has recently made the claim that the A^2 term does lead to a contribution greater than that of the $\mathbf{p} \cdot \mathbf{A}$ term. An examination of his calculation indicates that he used nonorthogonal atomic wave functions, so that his large result for the A^2 term is entirely spurious. We have further looked into the contribution from the A^2 term in the next order beyond the dipole approximation, that is, when the second term is retained in the expansion $e^{-2i\mathbf{k}\cdot\mathbf{r}} = 1 - 2i\mathbf{k}\cdot\mathbf{k} + \cdots$. The resulting approximate transition probability is a factor of about 2×10^{-5} smaller than that which arises from the p·A term alone. Furthermore, the cross term between $\mathbf{p} \cdot \mathbf{A}$ and A^2 gives a vanishing contribution to the total transition probability, so we need be concerned only with the first term in (1), which is also equivalent to the

$$H' = -e\mathbf{r} \cdot \mathbf{E}(0) \,. \tag{2}$$

II. PROCEDURE

Following standard perturbation methods, the transition probability per ion for a double-photon absorption (frequency ν_2) is

$$W_{2} = 4\pi^{2} \alpha^{2} m^{2} v \nu_{2}^{2} F^{2} V \frac{1}{2l_{i}+1} \sum_{m_{i}=-l_{i}}^{l_{i}} \int d\hat{k}_{f} \\ \times \left| \sum_{n} \frac{\langle i | \hat{e} \cdot \mathbf{r} | n \rangle \langle n | \hat{e} \cdot \mathbf{r} | f \rangle}{E_{n}-E_{i}-h \nu_{2}} \right|^{2}, \quad (3)$$

where, aside from the well-known atomic constants mand α , v is the velocity of the ejected electron, F is the photon flux, V is a normalizing volume for the continuum states, l_i and m_i are the orbital angular momentum quantum numbers of the initial one-electron state, $d\hat{k}_f$ is the element of solid angle into which the electron is ejected, and \hat{e} is a unit vector in the direction of polarization of the radiation. Our model is that of a one-electron transition from initial state $|i\rangle$ to final state $|f\rangle$ via intermediate state $|n\rangle$, in which all intermediate states and the final state are in the continuum and normalized such that

$$|n\rangle \xrightarrow[r=\infty]{} \frac{1}{\sqrt{V}} \left[e^{i\mathbf{k}_{n}\cdot\mathbf{r}} + \frac{e^{-ik_{n}r}}{r} \tilde{f}(\mathbf{r}) \right].$$
(4)

All one-electron transition probabilities will then be weighted according to the number of equivalent electrons which may be involved in the process and the statistical weights of the final states of the residual atom. All the one-electron states are taken to be eigenfunctions corresponding to an effective central field:

$$\left[-\nabla^2 + U(\mathbf{r}) - \boldsymbol{\epsilon}_n\right] |n\rangle = 0. \tag{5}$$

Our choice of potential U(r) is discussed later, in detail. All that should be mentioned now is that it is is chosen to yield a bound valence p state with binding energy equal to the observed electron affinity. In (5), if r is expressed in atomic units (a_0) , then U(r) and $\epsilon_n = (2m/\hbar^2)E_n$ are also in atomic units (Rydbergs).

In terms of this atomic model, the sum in (3),

$$S = \sum_{n} \frac{\langle i | \hat{\boldsymbol{e}} \cdot \mathbf{r} | n \rangle \langle n | \hat{\boldsymbol{e}} \cdot \mathbf{r} | f \rangle}{\epsilon_{n} - \epsilon_{i} - \epsilon_{\text{ph}}}, \qquad (6)$$

may be evaluated implicitly by the following method, due to Dalgarno and Lewis.⁵ (This method has been applied by Zernik⁶ to the double-quantum ionization of the hydrogen atom from its excited state.) Let us define the function

$$|M_{f}\rangle = \sum_{n'} \frac{|n'\rangle \langle n'|\hat{e} \cdot \mathbf{r}|f\rangle}{\epsilon_{n'} - \epsilon_{i} - \epsilon_{\mathrm{ph}}},$$
(7)

where the sum over n' is extended over the complete spectrum of the eigenfunctions of (5). This might include bound states lying below ϵ_i , which are excluded as intermediate states in the sum in (6) because they are filled by inner-shell electrons. Thus, we may write the desired sum as

$$S = \langle i | \hat{e} \cdot \mathbf{r} | M_f \rangle - \sum_j \frac{\langle i | \hat{e} \cdot \mathbf{r} | n_j \rangle \langle n_j | \hat{e} \cdot \mathbf{r} | f \rangle}{\epsilon_{n_j} - \epsilon_i - \epsilon_{\text{ph}}}, \qquad (8)$$

where n_j represents an occupied orbital. One can easily check by substitution that $|M_f\rangle$ satisfies the inhomogeneous differential equation

$$\left[-\nabla^{2}+U(\mathbf{r})-\epsilon_{i}-\epsilon_{\mathrm{ph}}\right]|M_{f}\rangle=\left(\hat{e}\cdot\mathbf{r}\right)|f\rangle.$$
(9)

In an equivalent manner, one may define the function $|M_i\rangle$:

$$|M_{i}\rangle = \sum_{n'} \frac{|n'\rangle \langle n'|\hat{e} \cdot \mathbf{r}|i\rangle}{\epsilon_{n'} - \epsilon_{i} - \epsilon_{\rm ph}},$$
(10)

satisfying

$$\left[-\nabla^{2}+U(\mathbf{r})-\epsilon_{i}-\epsilon_{\mathrm{ph}}\right]|M_{i}\rangle=(\hat{e}\cdot\mathbf{r})|i\rangle,\qquad(11)$$

from which it follows that

$$S^* = \langle f | \hat{e} \cdot \mathbf{r} | M_i \rangle - \sum_j \frac{\langle f | \hat{e} \cdot \mathbf{r} | n_j \rangle^* \langle n_j | \hat{e} \cdot \mathbf{r} | i \rangle^*}{\epsilon_{n_j} - \epsilon_i - \epsilon_{\text{ph}}}.$$
 (12)

As we wish to solve an inhomogeneous radial equation rather than an inhomogeneous partial-differential

⁴ E. Corinaldesi, Phys. Rev. Letters 15, 335 (1965).

⁵ A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) A233, 70 (1956); also see C. Schwartz, Ann. Phys. (N. Y.) 6, 156 (1959).

⁶ W. Zernik, Phys. Rev. **135**, A51 (1964); W. Zernick and R. W. Klopfenstein, J. Math. Phys. **6**, 262 (1965).

equation, we must make the angular resolutions

$$|i\rangle = \frac{w(r)}{r} Y_{l_i m_i}(\hat{r}),$$

$$|f\rangle = \frac{1}{\sqrt{V}} \sum_{L} i^L e^{-i\eta L} \frac{u_L(r)}{r} P_L(\hat{k}_f \cdot \hat{r}).$$

with the normalizations

$$\int_0^\infty w^2 dr = 1$$

and

$$u_L \xrightarrow[r \to \infty]{} \frac{2L+1}{k_f} \sin(k_f r - \frac{1}{2}L\pi + \eta_L),$$

where $k_f^2 = \epsilon_f$. If one makes these substitutions in (6), and takes the specific case of $l_i=1$, one obtains after some algebra the result

$$\frac{1}{3} \sum_{m_{i}} \int d\hat{k}_{f} |S|^{2} = \frac{16\pi^{2}}{9V} \left(\frac{2m}{\hbar^{2}}\right)^{2} \\ \times \left\{\frac{1}{27}(I_{01} - J_{01})^{2} + \frac{8}{135}(I_{01} - J_{01})(I_{21} - J_{21}) + \frac{34}{675}(I_{21} - J_{21})^{2} + \frac{12}{1225}(I_{23} - J_{23})^{2}\right\}.$$
(13)

Here, the radial matrix elements are

$$I_{01} = \langle wrv_{0}^{+} \rangle = \langle v_{0}ru_{1} \rangle,$$

$$I_{21} = \langle wrv_{2}^{-} \rangle = \langle v_{2}ru_{1} \rangle,$$

$$I_{23} = \langle wrv_{2}^{+} \rangle = \langle v_{2}ru_{3} \rangle,$$

$$J_{01} = \sum_{j} \frac{\langle wru_{0j} \rangle \langle u_{0j}ru_{1} \rangle}{\epsilon_{0j} - \epsilon_{i} - \epsilon_{ph}},$$

$$J_{21} = \sum_{j} \frac{\langle wru_{2j} \rangle \langle u_{2j}ru_{1} \rangle}{\epsilon_{2j} - \epsilon_{i} - \epsilon_{ph}},$$

$$J_{23} = \sum_{j} \frac{\langle wru_{2j} \rangle \langle u_{2j}ru_{3} \rangle}{\epsilon_{2j} - \epsilon_{i} - \epsilon_{ph}}.$$
(14)

The *I* matrix elements are the radial counterparts of the first terms in (8) and (12), while the *J*'s correspond to the second terms. The w and u_L functions have been defined as the bound and continuum radial wave functions in our central potential U(r), and the remaining functions above are the solutions of the following inhomogeneous equations:

$$\left[\frac{d^2}{dr^2} - U(r) - \frac{l(l+1)}{r^2} + \epsilon_i + \epsilon_{\rm ph}\right] {\binom{v_l^{\pm}}{v_l}} = r {\binom{u_{l\pm 1}}{w}}.$$
 (15)

All radial functions are real as is obvious from the specified asymptotic forms. The functions with subscript jare the lower lying bound s and d states. The contributions of these states to the intermediate state sum are explicitly included in the I's and must be subtracted out via the J's.

We have solved the inhomogeneous equation (15), with the solution made to vanish at the origin, and have evaluated the I matrix elements in the two alternate ways indicated. In most cases the two forms agreed to within 5%, which we take as a measure of the numerical accuracy in the solution of the homogeneous and inhomogeneous radial equations and the evaluation of the matrix elements. The contribution of the J's in every case was less than 1%, primarily because the energy denominators are large.

Having evaluated all the above radial functions for the two-photon absorption, it is a very simple matter to evaluate the radial matrix elements $\langle wru_0 \rangle$ and $\langle wru_2 \rangle$ which enter the single-photon absorption cross section. The single-photon absorption to the same final state $|f\rangle$ occurs at twice the photon frequency $\nu_1 = 2\nu_2$. This cross section in the same atomic model is

$$\sigma_1 = \alpha \frac{m^2}{\hbar^2} v \nu_1 V \frac{1}{2l_i + 1} \sum_{m_i} \int d\hat{k}_f |\langle i| \hat{e} \cdot \mathbf{r} |f\rangle|^2.$$
(16)

Also we need to evaluate the continuum functions u_L for L=0, 1, 2, and 3, and these contain the scattering phase shifts η_L . The total elastic-scattering cross section from the parent neutral atom,

$$Q_{\text{clastic}} = \frac{4\pi}{k^2} \sum_{L=0}^{3} (2L+1) \sin^2 \eta_L, \qquad (17)$$

is evaluated for an energy range in which L>3 is unimportant.

The quantities defined in (16) and (3) apply to the single- and double-photon absorption of a one-electron system. They must be multiplied by the number of equivalent electrons in the valence shell of the negative ion. Furthermore, the residual atom may be left in a number of different final states of the same configurations. The halogens may be left in the ${}^{2}P_{3/2}$ or ${}^{2}P_{1/2}$ state while O and S may be in either the ${}^{3}P_{2,1,0}$, ${}^{1}D_{2}$, or ${}^{1}S_{0}$ states. Similarly, C and Si may go to the ${}^{3}P_{0,1,2}$ final states only because we assume that the only stable negative-ion state of these atoms is the 4S state. Thus, excited doublet state of the p^3 configuration of C and Si are not accessible in a radiative process. The finestructure splitting in the initial ${}^{2}P$ state of O⁻ is ignored. All of the averaging over final states is done according to their statistical weights 2J+1, and the ejected electron's kinetic energy ϵ_f is accordingly changed for each residual atom state.

Ion	(a_0)	$\stackrel{\alpha}{(a_0^3)}$	^{еі} (Ry)	$r_0 (a_0)$	Onset energies (Ry) of final states of the residual atom
c-	1.5	14.2ª	-0.09188d	1.092	$0({}^{3}P_{0}), 0.00015({}^{3}P_{1}), 0.00040({}^{3}P_{2})$
0-	1.5	5.19ª	-0.10770	1.098	$0({}^{3}P_{2}), 0.00144({}^{3}P_{1}), 0.00206({}^{3}P_{0}),$
					$0.1446({}^{1}D_{2}), 0.3079({}^{1}S_{0})$
F-	1.5	4.05ª	-0.2534f	1.154	$0({}^{2}P_{812}), 0.00368({}^{2}P_{112})$
Si ⁻	2.5	47.2 ^b	-0.1022s	2.048	$0({}^{3}P_{0}), 0.00070({}^{3}P_{1}), 0.00203({}^{3}P_{2})$
s-	2.5	17.5 ^b	-0.1521h	1.758	$0({}^{3}P_{2}), 0.00362({}^{3}P_{1}), 0.00523({}^{3}P_{0}),$
					$0.08417 ({}^{1}D_{2}), 0.2021 ({}^{1}S_{0})$
C1-	2.5	23.5°	-0.2656f	1.818	$0({}^{2}P_{3l2}), 0.00803({}^{2}P_{1l2})$
Br-	3.5	24.9°	-0.2472^{f}	2.110	$0({}^{2}P_{8l2}), 0.03357({}^{2}P_{1l2})$
I-	4.5	40.5°	-0.2248 ⁱ	2.400	$0({}^{2}P_{3l2}), 0.06927({}^{2}P_{1l2})$

TABLE I. Parameters used in atomic models.

^a Taken from A. Dalgarno, Advan. Phys. 11, 281 1962.
^b Chosen such that α(Si)/α(C) = α(S)/α(O) = α(Cl)/α(F).
^a These values are assumed, such that they are, larger than the neighboring rare-gas polarizability.
^d M. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962).
^e L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. 115, 504 (1958).
^f R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963).
^g E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. 133, A1274 (1964).
^b L. M. Branscomb and S. J. Smith, J. Chem. Phys. 25, 598 (1956).
ⁱ B. Steiner, M. L. Seman, and L. M. Branscomb, Phys. Rev. 37, 1200 (1962); Atomic Collision Processes (North-Holland Publishing Company, Amsterdam, 1963), p. 537.

III. POTENTIAL FUNCTION AND RESULTS

The potential function which we have adopted is

$$U(r) = H_{\rm HS}(r) + \frac{2}{r} (1 - e^{-r/r_0}) - \alpha \frac{(1 - e^{-r/r_p})}{(r_p^2 + r^2)^2}, \quad (18)$$

where $U_{\rm HS}$ is the Hartree-Fock-Slater potential for the neutral atom as evaluated by the methods of Herman and Skillman,⁷ where the second term removes the Coulomb tail of $U_{\rm HS}$, and where the third term introduces the effect of polarization. The functional form of the polarization term was chosen such that the term vanishes as $r \to 0$ and $\to (-\alpha/r^4)$ as $r \to \infty$. The parameter r_p was arbitrarily chosen to be 1.5, 2.5, 3.5, 4.5, respectively, for all atoms in each of the successive



FIG. 1. Double-quantum transition probability for I⁻. Presently calculated—solid line; plane-wave approximation of Ref. 2—dashed line; the experimental point is obtained in Ref. 1. The coherence correction factor of $\frac{2}{3}$ applied in Ref. 1 is not applicable here [J. L. Hall (private communication)].

⁷ F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).



FIG. 2. Single-photon photodetachment cross sections for C⁻, O⁻, and I⁻. Presently calculated—solid lines; experimental results—dashed lines [C⁻, Ref. d, Table I; O⁻, L. M. Branscomb, S. J. Smith, and G. Tisone, J. Chem. Phys. 43, 2906 (1965); I⁻, Ref. i, Table I].

rows of the periodic table. The atomic polarizability α is chosen as the best possible from the experimental and theoretical literature. The value of the remaining parameter r_0 is chosen so that the resulting potential will support an np valence state with binding energy equal to the best known binding energy of the negative ion. The Schrödinger equation program (SCHEQ) in Ref. 7 is used to search for r_0 . The potential parameters and binding energies used in the calculation are given in Table I. Also given are the ejected-electron energy values at which a new residual atom state may be excited.

The results for the double-quantum absorption of I⁻ are plotted in Fig. 1. The quantity plotted is W_2/F^2 , where F is a dimensionless quantity numerically equal to the photon flux in photons/cm² sec. We express all the calculated quantities as functions of k_f^2 , the ejectedelectron energy in Rydbergs. In order to obtain the appropriate photon frequency, one must use $h\nu_1/Ry$

TABLE II. Double-quantum transition probabilities W_2/F^2 (in 10⁻⁵⁰ sec⁻¹.)

kf ² (Electron energy in Ry)	с-	0-	F-	Si-	s-	C1-	Br-	I-
0.005	12.3	3.76	0.258	14.5	2.10	0.637	1.11	1.96
0.010	26.8	9.28	0.763	44.8	6.09	1.68	2.83	5.00
0.015	37.2	13.8	1.32	70.9	10.4	3.10	4.62	8.11
0.020	43.4	17.1	1.86	89.6	14.2	4.54	6.28	10.9
0.025	46.4	19.1	2.35	101.0	17.3	5.88	7.75	13.3
0.03	47.1	20.2	2.79	107.0	19.5	7.07	8.99	15.3
0.05	41.0	19.6	3.93	102.0	22.8	10.1	14.3	19.8
0.07	31.5	16.6	4.35	90.0	21.6	11.1	17.3	20.6
0.09	•••	12.3	4.35		19.6	11.1	17.9	24.6
0.11	•••	•••	4.15	•••	23.8	10.5	17.3	26.4
0.13	•••	•••	3.86	• • •	25.4	9.85	16.4	26.3
0.15	•••	•••	3.55	• • •	•••	9.14	15.5	25.5
0.17	•••	•••	3.25	• • •	• • •	8.47	14.7	25.0
0.19	•••	•••	2.97	•••		7.89	14.0	
0.21	•••	•••	2.67	•••	•••	7.45	13.1	•••

TABLE III. Single-quantum photodetachment cross sections σ_1 (in 10⁻¹⁸ cm²).

<i>kf</i> ² (Electron energy in Ry)	C-	0-	F-	Si-	s-	CI-	Br-	I-
0.005	7.18	4.08	2.93	26.2	6.49	6.98	12.9	16.3
0.01	8.82	5.37	4.29	27.4	9.27	10.9	13.8	16.6
0.02	10.0	6.42	5.45	25.6	11.2	13.7	13.8	16.3
0.03	10.5	6.84	6.16	24.9	11.7	14.3	13.6	16.3
0.05	11.4	7.27	6.76	27.1	12.4	14.8	21.5	17.5
0.07	12.4	7.63	7.09	32.0	13.4	15.5	22.1	27.0
0.09	13.3	7.98	7.35	37.4	14.8	16.6	23.7	34.6
0.11	14.1	8.31	7.61	42.2	25.8	18.0	26.1	39.3
0.13	14.8	8.61	7.89	46.2	27.6	19.8	29.0	45.2
0.15	15.4	14.5	8.19	49.2	29.5	21.6	32.3	52.0
0.17	15.9	16.8	8.49	51.4	31.5	23.6	35.6	59.1
0.19	16.2	17.0	8.80	53.0	33.7	25.6	38.9	66.0
0.21	16.5	17.1	9.11	53.9	35.7	27.7	42.0	72.5
0.23	16.7	17.2	9.41	54.4	37.7	29.7	44.9	78.3
0.25	16.8	17.3	9.70	54.4	39.5	31.6	47.6	83.5
0.3	16.9	17.5	10.4	52.6	46.0	36.3	53.5	92.8
0.4	16.6	19.6	11.4	42.8	52.0	44.3	61.5	97.7
0.5	16.0	18.9	12.1	30.4	54.4	50.3	64.9	89.0
0.6	15.1	18.1	12.6	20.1	53.5	54.0	63.6	73.3
0.7	14.1	17.3	12.8	12.8	49.8	54 .6	58.2	56.4
0.8	13.1	16.4	12.8	7.82	43.6	51.6	50.1	41.6
0.9	12.1	15.6	12.8	4.64	35.6	44.9	41.1	30.2

 $=2h\nu_2/\mathrm{Ry}=|\epsilon_i|+k_f^2$. The experimental value¹ for the double-photon transition rate in I^- at the ruby-laser wavelength is also shown in Fig. 1. Its error bar is primarily the result of uncertainty in the mode of oscillation of the laser. The present result is seen to fall just below the error bar. The plane-wave approximation of Ref. 2 is also plotted. Table II contains W_2/F^2 for all the ions treated. Our method of solution of the inhomogeneous Eqs. (15) requires that $\epsilon_i + \epsilon_{\rm ph} < 0$, which means that it is not applicable for $h\nu_2/Ryd \ge |\epsilon_i|$, or for frequencies for which single-photon absorption is possible.

In Fig. 2 the presently computed single-photon photodetachment cross sections are compared with the experimental results for C⁻, O⁻, and I⁻. The quality of agreement varies from ion to ion. In I⁻ our computed curve is about 20% below the measured points, with good agreement between their shapes. In O⁻ the agreement in shape is also reasonably good, but up to the excitation threshold of the ^{1}D state the calculated magnitude is about 25% above experiment. The larger discrepancy above this threshold may reflect the fact that the polarizability of the oxygen atom in the ^{1}D state is not the same as its ground state value, while our calculation keeps the same α in U(r). In C⁻, the agreement between the shapes of the curves is poorer. The reason for this is not clear. Perhaps, since this is the lightest atom studied, one should expect the largest errors to occur for it with a static-field model; or possibly this is a result of lits being farthest removed from a closed-shell structure. Our curves for σ_1 are very much like those

TABLE IV. Electron-atom elastic scattering cross sections Q_{elastic} (in 10⁻¹⁶ cm²).

k ² (Electron energy in Ry)	С	0	F	Si	s	Cl	Br	I
0.005	0.683	1.19	0.149	58.8	2.47	7.90	44.0	60.0
0.01	1.55	1.62	0.314	24.8	0.736	4.04	22.9	28.0
0.05	6.07	3.64	1.28	3.61	2.51	0.847	1.94	3.87
0.11	9.52	5.36	2.24	16.9	7.91	3.66	5.04	11.8
0.15	10.7	6.05	2.73	24.7	10.7	5.66	8.23	17.7
0.21	11.7	6.71	3.30	33.6	14.0	8.33	12.5	25.0
0.25 0.3	12.1 12.3	6.98 7.20	3.60 3.91	38.0 42.2	15.6 17.4	9.87 11.6	$14.9 \\ 17.5$	$29.0 \\ 33.1$
0.4	12.4	7.39	4.35	47.2	20.1	14.5	21.5	38.9
0.5	12.2	7.40	4.63	48.4	22.5	17.0	24.5	41.8
0.6	12.0	7.32	4.80	47.0	24.7	19.6	26.7	42.3
0.7	11.7	7.19	4.90	44.1	26.8	22.1	28.1	41.1
0.8	11.4	7.04	4.95	40.7	28.2	24.2	28.7	39.5
0.9	11.1	6.87	4.96	37.3	28.7	25.6	28.6	38.0

obtained by Cooper and Martin⁸ by similar methods. A similar result for C⁻ has been obtained with Hartree-Fock wave functions.⁹ The results for σ_1 for all the ions treated are given in Table III. A measured value of $\sigma_1 = (3.3 \pm 2.0) \times 10^{-18}$ for F⁻ by Berry and Reimann (Ref. f, Table I) at $k_f^2 = 0.005$ is in good agreement with our calculated value of 2.93×10⁻¹⁸ cm². Berry, Reimann, and Spokes¹⁰ have also determined σ_1 for Cl⁻ to be $(15_{-5}^{+12}) \times 10^{18}$ cm² at $k_f^2 = 0.0064$, which is to be compared with our value of 6.98×10^{-18} cm² at $k_f^2 = 0.005$. They have also found σ_1 for Br⁻ to be $12(\pm 60\%) \times 10^{-18}$ cm² at $k_f^2 = 0.0064$, which also compares favorably with our value of 12.9×10^{-18} cm² at $k_f^2 = 0.005.$

The elastic-scattering cross sections are given in Table IV. The calculated values for oxygen are in good agreement with the recent experimental atomic-beam measurements of Sunshine, Aubrey, and Bederson.¹¹ Note that a Ramsauer minimum, much as is observed in the neighboring rare-gas atoms, is expected for the atoms Si, S, Cl, Br, and I. We do not find a Ramsauer minimum for F, which is consistent with its not being observed in experiments on Ne.

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⁸ J. W. Cooper and J. B. Martin, Phys. Rev. **126**, 1482 (1962). ⁹ V. P. Myerscough and M. R. C. McDowell, Monthly Notices Roy. Astron. Soc. **128**, 287 (1964). ¹⁰ R. S. Berry, C. W. Reimann, and G. N. Spokes, J. Chem. Phys. **37**, 2278 (1962). ¹¹ G. Sunshine, B. B. Aubrey, and B. Bederson, in *Proceedings of* the Event International Conference on the Physics of Electronic and

the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965 (Science Bookcrafters, Hastingson-Hudson, New York, 1965), p. 130.