O'Malley, and L. Spruch, Phys. Rev. 137, A1068 (1965).

[5] See M. J. Seaton, Monthly Notices Roy. Astron. Soc. 118, 504 (1958); M. J. Seaton, Proc. Phys. Soc. (London) 88, 801 (1966); M. Weinberg, Ph.D. thesis, University of Chicago, 1967 (unpublished); M. Weinberg, R. S. Berry, and J. Tully, J. Chem. Phys. 49, 122 (1968).

[6] M. M. Klein and K. A. Brueckner, Phys. Rev. 111, 1115 (1958); see also E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967); W. R. Garrett and H. T. Jackson, Jr., Phys. Rev. 153, 28 (1967) and J. W. Cooper and J. B. Martin, Phys. Rev. 123, 1482 (1962), for other calculations of the photodetachment cross section of O$^-$.

[7] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. 127, 1618 (1962).

[8] J. C. Tully, Ph.D. thesis, University of Chicago (1968) (unpublished).

[9] B. Friedman, Principles and Techniques of Applied Mathematics (John Wiley & Sons, Inc., New York, 1956), pp. 169–172.

[10] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. 111, 504 (1958).

[11] E. Brown, Phys. Rev. 126, 421 (1962).

[12] J. C. Slater, Quantum Theory of Atomic Structure (McGraw-Hill Book Company, Inc., New York, 1960), pp. 229–232.

[13] I. V. Abarenkov and V. Heine, Phil. Mag. 12, 529 (1965).

[14] I. V. Abarenkov and I. M. Antonova, Phys. Stat. Solids 20, 643 (1967).

PHYSICAL REVIEW VOLUME 182, NUMBER 1 5 JUNE 1969

Pseudopotential Method for Inelastic Processes in Atoms and Molecules. II. Photoionization of N_2[†]

Barry Schneider[*] and R. Stephen Berry
Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois 60637

(Received 23 December 1968)

The pseudopotential method developed in Paper I is applied to the photoionization of N_2. From the known quantum defects of two Rydberg series of N_2, we obtain the phase shifts of the photoionized electron. These phase shifts are used to construct a simple model potential approximation to the true pseudopotential. The model wave functions are then orthogonalized to the known Hartree-Fock wave functions of the N_2^+ core. Using these wave functions we calculate the total and differential cross section for photoionization of electrons from N_2 as a function of the energy of the outgoing electron. The results of the calculation are discussed and compared with some of the more recent experimental measurements of the aforementioned quantities.

I. INTRODUCTION

The photoionization of N_2 has been the subject of intensive efforts in a large number of laboratories during the past ten years. This work culminated in experimental measurements of the total cross section for the photoionization of electrons from N_2 as a function of incident light energy.[1–4] Quite recently the angular distribution of the photoelectrons from N_2 has been studied for formation of specific electronic states of the ion.[5]

The electronic structure of the N_2 molecule may be represented as

$$(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2)\ {}^1\Sigma_g^+ \qquad (1)$$

in the molecular orbital picture. The photoionization process with the lowest threshold energy

$$N_2({}^1\Sigma_g^+) + h\nu \rightarrow N_2^+({}^2\Sigma_g^+) + e \qquad (2)$$

begins to occur at an energy of 15.58 eV (795.9 Å). Using the selection rules for dipole radiation, we find that the only allowed states of the outgoing electron are $k\sigma_u$ and $k\pi_u$. The corresponding configurations and states of the $e - N_2^+$ system may be represented as

$$(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g k\sigma_u)\ ,\quad {}^1\Sigma_u^+ \qquad (3)$$

and

$$(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g k\pi_u)\ ,\quad {}^1\Pi_u\ ,$$

where k is the wave number of the escaping electron. As the energy of the photons is increased, channels corresponding to excited core N_2^+ states are opened. Thus at an energy of 16.69 eV (742.7 Å), we get

$$N_2(^1\Sigma_g^+) + h\nu \rightarrow N_2^+(^2\Pi_u) + e \tag{4}$$

and at 18.76 eV (661.0 Å)

$$N_2(^1\Sigma_g^+) + h\nu \rightarrow N_2^+(^2\Sigma_u^+) + e \ . \tag{5}$$

Our calculations stop short of the 18.76 eV threshold for the formation of the ($^2\Sigma_u^+$) second excited state of N_2^+.

The allowed states of the outgoing electron in Eq. 4 are $k\sigma_g$, $k\pi_g$, or $k\delta_g$. The total configurations and states corresponding to these outgoing 1-electron states are, respectively,

$$\begin{aligned} &(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^3 3\sigma_g{}^2 k\sigma_g) \ , \quad {}^1\Pi_u \ ; \\ &(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^3 3\sigma_g{}^2 k\pi_g) \ , \quad {}^1\Sigma_u^+ \ , \end{aligned} \tag{6}$$

and

$$(1\sigma_g{}^2 1\sigma_u{}^2 2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^3 3\sigma_g{}^2 k\delta_g) \ , \quad {}^1\Pi_u \ .$$

We can identify the two continuum states characteristic of the primary photoionization process as the limits of two well-known Rydberg series. The $^1\Sigma_u^+$ state can be considered as the ionization limit of the well known Worley-Jenkins[6] series, while the $^1\Pi_u$ state is the limit of a series recently identified by Carroll and Yoshino.[7] The Rydberg series converging to the $^2\Pi_u$ state of the N_2^+ ion are less well known experimentally. It can be established, however, that the first of the three states listed in expression (6) belongs to Worley's third Rydberg series.[8] There is enough data on the quantum defects[9] of these Rydberg series to get information on the low-energy phase shifts of the outgoing electron. Consequently we can do a simple pseudopotential calculation for the wave function of the continuum electron.

Before turning to the actual details of the calculation, let us consider some of the more recent experimental measurements of the N_2 photoionization cross section.

Perhaps the absolute cross-section data with the highest resolution is that of Cook and Metzger.[2] Examination of their absorption curves shows a sharp rise at the 795.9 Å threshold, followed by a succession of fairly well-defined peaks at shorter wavelengths, down to about 725 Å. Below 725 Å, the cross section is relatively smooth, containing only three or four clearly resolved peaks. The occurrence of such detailed structures in the cross section at low energies can only be explained by the formation of a long-lived state. Because the structure is observed in both the absorption and ionization cross sections, the presumed cause of the structure is autoionization. It is now well established that the major contribution to the photoionization cross section of H_2 at energies up to 2 eV above the ionization threshold is from autoionizing states.[10] The autoionization of these states is a result of the breakdown of the Born-Oppenheimer approximation in molecules.[11] In effect, an electron initially excited by light into a Rydberg state of the molecule slowly exchanges energy with the nuclei. If enough energy is available in the nuclear motion to raise the Rydberg electron to the continuum, the molecule may eventually ionize.

Naturally a comparison of experimental and theoretical cross sections for direct photoionization depends on the resolution of the experimental curve; only if the autoionization peaks are well resolved can one distinguish the continuous background unambiguously. The published data of Cook and Metzger[2] do not allow us to decide whether the direct and autoionization contributions are distinguishable. However, recent relative cross-section measurements of Berkowitz and Chupka,[12] made with very high resolution, do clearly separate the peaks. The relative intensities of the maxima and minima in cross sections of Cook and Metzger agree well with those of Berkowitz and Chupka, so that we have reasonable confidence in the estimated continuous contribution in Cook and Metzger's data.

When one calculates elastic scattering cross sections, one often computes differential cross sections to be compared with experiment. Photoionization offers no exact analog to the usual differential scattering cross section because the angular distribution of photoelectrons from a set of atoms or randomly oriented molecules is essentially of the form $I(\theta) = \alpha + \beta \cos^2\theta$.[13,14] However, the coefficients α and β are functions of energy and of the transition dipole matrix elements connecting initial and final states. In principle it is possible to identify final states (and, by implication, initial 1-electron states) by comparing experimental values of α and β with corresponding theoretical values for various hypothesized transitions. It is also possible to determine phenomenologically the upper and lower limits of α/β for specific molecular ionization processes. We have determined α/β numerically from our theoretical model and have considered the limits it may have for the formation of N_2^+ in its $^2\Sigma_g^+$ ground state. These results, at best, are only in fair argument with the measurements of Ehrhardt, Berkowitz, and Tekaat. One reason for the discrepancy is presumably due to the limitation of our theory at energies well above ionization thresholds. A photoionization experiment is suggested for the energy range for which the theory is most nearly valid.

II. THEORY

We now apply the pseudopotential method described previously to the problem of photoionization of N_2. Consider a beam of photons incident on a molecule with a fixed orientation in space. We ignore any effects of the radiation field on the molecular wave function aside from the lowest-order one-electron absorption process of immediate interest. The total wave function of the continuum eigenstate in the asymptotic region of the coordinate $\vec{r}_N$ of the photoionized electron (electron N) can be written as

$$\lim_{r_N\to\infty} \Psi_{qlm}(\vec{r}_1\ldots\vec{r}_N;R)=k_q^{-1/2}r_N^{-1}\phi_q(\vec{r}_1\ldots\vec{r}_{N-1};R)Y_{lm}(\hat{r}_N')\exp(i\zeta_{ql})$$

$$-\sum_{q'l'} S^{\dagger}(ql;q'l'm)k_q^{-1/2}r_N^{-1}\phi_{q'}(\vec{r}_1\ldots\vec{r}_{N-1};R)Y_{l'm}(\hat{r}_N')\exp(i\zeta_{q'l'})\ , \quad (7)$$

where the matrix $S^{\dagger}$ is the adjoint of the scattering matrix in the angular momentum representation. The other quantities in Eq. 7 are defined in standard fashion as

$\zeta_{ql}=k_q r_N-\frac{1}{2}l\pi-\gamma_q \ln 2k_q r_N+\sigma_l$, $\vec{k}_q$ = wave vector of the photoionized electron.

$\sigma_l=\operatorname{Arg}\Gamma(l+1+i\gamma q)$ = the Coulomb phase shift, (8)

$\phi_q(\vec{r}_1\ldots\vec{r}_{N-1};R)$ = a bound state of the molecule-ion, and R = internuclear distance.

The primes on the arguments of the spherical harmonics indicate we have chosen a coordinate system centered at the midpoint of the molecule with its z axis along the internuclear axis. The signs of $k_q r$ in the asymptotic form of Ψ_{qlm} are consequences of the fact that we are dealing with a sort of time-reversed scattering process and must use the Ψ^-, rather than the Ψ^+ wave function for the overall state of the system.[15] If we specialize to the one-state approximation we get

$$\lim_{r_N\to\infty} \Psi_{qlm}(\vec{r}_1\ldots\vec{r}_N;R)=k_q^{-1/2}r_N^{-1}\phi_q(\vec{r}_1\ldots\vec{r}_{N-1};R)\{Y_{lm}(\hat{r}_N')\exp(i\zeta_{ql})[1-S^{\dagger}(ql;qlm)]$$

$$-\sum_{l'} S^{\dagger}(ql;ql'm)Y_{l'm}(\hat{r}_N')\exp(i\zeta_{ql'})\}\ . \quad (9)$$

As one would expect for an axially symmetric system, there is coupling among the partial waves. This coupling is a direct consequence of the form of the molecular potential in the core region of the system and the boundary conditions placed on the wave function at infinity. It can be shown, however, that at low energies, the S matrix may be transformed by a real orthogonal matrix to *approximately* uncouple the partial waves at infinity. The wave functions obtained by this transformation are approximately eigenfunctions of $\mathcal{L}^2$ in the asymptotic region. Within the core, they are still linear combinations of spherical harmonics. On the basis of the low amplitude of the pseudofunction in the core, as discussed in I, coupling in the inner region should be much less important to the pseudowave function than to the actual continuum function. The pseudowave function is kept out of the core to a much greater degree by the effective potential of the core electrons, and particularly by that part arising from the exclusion principle. The molecular pseudopotential method is based on the conjecture that most of the nonspherical effects in the continuum function are contained in the conditions that this function be orthogonal to the wave functions of all states of the same symmetry and lower energy. Thus we assume that the model potential has the form of a constant for a given l, m, and E in the core region,

$$V_m=C_{lm}(E),\ \text{for}\ r<r_c;\quad V_m=-Zr^{-1},\ \text{for}\ r>r_c\ . \quad (10)$$

Such a model potential should be almost as good an approximation to the molecular pseudopotential as its counterpart was for the atomic case, at least for states of low energy. The eigenfunctions of the Hamiltonian

$$\mathcal{H}_0=-(\hbar^2/2m_e)\nabla^2+V_m \quad (11)$$

are quite simple. If we define as case I

$$K^2=k^2-2C_{lm},\ \text{when}\ k^2-2C_{lm}>0,\ \text{zero always} \quad (12a)$$

or as case II

$$K^2 = 2C_{lm} - k^2, \quad \text{when } k^2 - 2C_{lm} < 0, \tag{12b}$$

we have for $r < r_c$,

$$\phi_0^m = A_{lm} j_l(Kr) Y_{lm}(\hat{r}'), \quad \text{Case I;} \quad \phi_0^m = A_{lm} I_l(Kr) Y_{lm}(\hat{r}'), \quad \text{Case II;} \tag{13a}$$

and for $r > r_c$,

$$\phi_0^m = B_{lm} Y_{lm}(\hat{r}')(kr)^{-1}[F_l(kr) + \tan\delta_{lm} G_l(kr)] \ . \tag{13b}$$

We define j_l as the ordinary spherical Bessel function, I_l the spherical hyperbolic Bessel function, F_l the regular spherical Coulomb function, and G_l the irregular spherical Coulomb function. The short-range part of the phase shift δ_{lm} is obtained by using the Quantum Defect Method as extended to molecules by Weinberg.[16] When a value of r_c is chosen, the corresponding value of k may be obtained as in the atomic case by applying the continuity conditions

$$A_{lm} j_l(Kr_c) = B_{lm}[F_l(kr_c) + \tan\delta_{lm} G_l(kr_c)](kr_c)^{-1} \ ,$$

$$A_{lm} \frac{d}{dr} j_l(Kr)\bigg|_{r=r_c} = B_{lm} \frac{d}{dr}\left[\frac{F_l(kr) + \tan\delta_{lm} G_l(kr)}{kr}\right]_{r=r_c} \quad \text{(Case I);} \tag{14a}$$

$$[\text{Similarly with } j_l(kr) \text{ replaced by } I_l(kr)] \ . \qquad \text{(Case II)} \tag{14b}$$

Since the normalization constant B_{lm} is quite arbitrary, we choose it to be

$$B_{lm} = k^{1/2} \cos(\delta_{lm}) 2i \exp(-i\delta_{lm}) \ .$$

To get the total wave function we orthogonalize our model function to the occupied bound states of the molecule-ion, multiply the result by all the other spin orbitals of the system and antisymmetrize the resultant product. The asymptotic form of the total wave function given by the above procedure may be written as

$$\lim_{r_N \to \infty} \Psi_{qlm}(\vec{r}_1 \ldots \vec{r}_N; R) = 2ik_q^{-1/2} r_N^{-1} \exp(-i\delta_{lm}) Y_{lm}(\hat{r}_N') \phi_q(\vec{r}_1 \ldots \vec{r}_{N-1}; R) \sin(\zeta_{ql} + \delta_{lm})$$

$$= k_q^{-1/2} r_N^{-1} Y_{lm}(\hat{r}_N') \phi_q(\vec{r}_1 \ldots \vec{r}_{N-1}; R)[\exp(i\zeta_{ql}) - \exp(-i\zeta_{ql} - 2i\delta_{lm})] . \tag{15}$$

Thus we can identify

$$S^{\dagger}(ql; qlm) = \exp(-2i\delta_{lm}) \ .$$

The function (15) is not the proper wave function to be used to calculate the differential or total photoionization cross section. It does not have the proper behavior at long distances from the nuclei. The correct continuum wave function for calculation of photoionization must differ from a pure Coulomb wave in containing only incoming spherical Coulomb waves in the asymptotic region. This is not a difficulty which need be of much concern because it is a relatively simple matter to construct the correct wave function from the Ψ_{qlm}. Since the core eigenfunction and antisymmetrizer play no essential part in what follows, we shall leave them implicit in our wave functions. Thus, we write

$$\Psi^- = \sum_{l,m} a_{lm} Y_{lm}^*(\hat{k}_q') \Psi_{qlm}(\vec{r}_N) \tag{16}$$

in the molecular coordinate system. Recalling the expansion of a Coulomb wave in spherical harmonics we have

$$\Psi_c^- = (\pi^{-1} 2kq)^{1/2} \sum_{l,m} i^l Y_{lm}^*(\hat{k}_q') Y_{lm}(\hat{r}_N')(k_q r_N)^{-1} \exp(-i\sigma_l) F_l(k_q r_N) \ ,$$

$$= (\pi^{-1} 2k_q)^{1/2} \sum_{l,m} i^l Y_{lm}^*(\hat{k}_q) Y_{lm}(\hat{r}_N)(k_q r_N)^{-1} \exp(-i\sigma_l) F_l(k_q r_N) \ . \tag{17}$$

Either form is acceptable of the rotational invariance of the pure Coulomb wave. Letting r_N approach infinity, we have for the difference of the two waves

$$\lim_{r_N \to \infty} (\Psi^- - \Psi_c^-) = \sum_{l,m} k_q^{-1/2} r_N^{-1} Y_{lm}^*(\hat{k}'_q) Y_{lm}(\hat{r}'_N)$$

$$\times \{a_{lm}[\exp(i\zeta_{ql}) - \exp(-i\zeta_{ql} - 2i\delta_{lm})] - i^{l-1}\pi^{-1/2}\exp(-i\sigma_l)[\exp(i\zeta_{ql}) - \exp(-i\zeta_{ql})]\}. \tag{18}$$

To make the outgoing spherical Coulomb waves vanish, we choose

$$a_{lm} = (2\pi)^{-1/2} i^{l-1} \exp(-i\sigma_l) . \tag{19}$$

This is the desired result. The final expression for the wave function is

$$\Psi^- = (2\pi)^{-1/2} \sum_{l,m} i^{l-1} \exp(-i\sigma_l) Y_{lm}^*(\hat{k}'_q) \Psi_{qlm}(\vec{r}_N) . \tag{20}$$

In order to transform the description of the photoionization process from the molecular system to the laboratory system, we use the relationship

$$Y_{lm}(\hat{x}') = \sum_{m'} D^l_{m'm}(\alpha,\beta,\gamma) Y_{lm'}(\hat{x}) . \tag{21}$$

This allows us to transform the total wave function into

$$\Psi^- = (2\pi)^{-\frac{1}{2}} \sum_{l,m,m'} i^{l-1} \exp(-i\sigma_l) D^{l*}_{m'm}(\alpha,\beta,\gamma) Y^*_{lm'}(\hat{k}_q) \Psi_{qlm} . \tag{22}$$

The $D^l_{mm'}$ are the generalized spherical functions as defined by Rose.[14] The orientation of the molecular axis relative to the laboratory axis is given by the Euler angles α, β, and γ defined according to the conventions of Rose.[17] The formula for the differential cross section for photoionization of electrons diatomic molecules has recently been derived by Tully, Berry, and Dalton[13] within the context of the Born-Oppenheimer approximation. The photoionization cross section for an ensemble of fixed, randomly oriented molecules is

$$\sigma_q(\Omega) = (2\pi e^2 \hbar^2)(m_e^2 cv)^{-1} \sum_{l,m,\lambda,\mu} (-1)^{m_q + m_I} (4\pi)^{-1} [(2l+1)(2\lambda+1)]^{\frac{1}{2}} A_{lmm_q m_I} A^*_{\lambda\mu m_q m_I} \tag{23}$$

$$\times \sum_{J=0,2} (2J+1)^{-1} C(11J \,|\, m_I - m - m_q, \mu + m_q - m_I) C(11J \,|\, 00) C(l\lambda J \,|\, 00) C(l\lambda J \,|\, m, -\mu) P_J(\cos\theta),$$

where m_I is the m quantum number of the initial state, m_q is the m quantum number of the residual core, the $C(l\lambda J|\, m_l m_\lambda)$ are the Clebsch-Gordan coefficients,[17] P_J $(\cos\theta)$ is the Legendre Polynomial of Jth order, and

$$A_{lmm_q m_I} = 2\pi m_e v \hbar^{-1} i^{-l+1} (\tfrac{2}{3})^{\frac{1}{2}} \exp(i\sigma_l) d(lmm_q m_I) ,$$

$$d(lmm_q m_I) = \left[\sum_{j=1}^{N} \int d\vec{r} d\vec{R} \Psi^*_{qlm} r_j Y_{1m''}(\hat{r}'_j) \Psi_I \right]_{m'' = m + m_q - m_I} . \tag{24}$$

The integrations in $d(lmm_q m_I)$ are taken over both electronic and nuclear coordinates. The significant point to notice about the above expression is its form

$$\sigma_q(\Omega) = \alpha + \beta \cos^2\theta \quad , \tag{25}$$

which is exactly what one obtains for atoms with randomly oriented angular momenta. Of course α and β do not have the same meaning for molecules as they do for atoms owing to the noncentral character of the molecular potential. To obtain the total cross section, we integrate over Ω:

$$\sigma_q^{\text{total}} = (2\pi e^2 \hbar^2)(3m_e^2 cv)^{-1} \sum_{l,m} |A_{lmm_q m_I}|^2 = (16\pi^3 e^2 v)(9c)^{-1} \sum_{l,m} |d(lmm_q m_I)|^2 . \tag{26}$$

Having derived all the expressions necessary for the evaluation of the wave functions and cross sections of interest, we can proceed to the details of the calculation.

Using the known quantum defects for the rydberg series converging to the ${}^2\Sigma_g^+$ state of N_2^+, we computed the phase shifts for the $k\sigma_u$ and $k\pi_u$ continuum electrons for a number of values of k. The quantum defects are given in Table II. From the phase shifts and the continuity conditions of Eq. 14, the model wave functions were derived. Explicitly, we have, for $r<r_c$,

$$\begin{aligned}\phi_0{}^m(k\sigma_u) &= A_{10}j_1(kr)Y_{10} = A_{10}[(\sin kr)/k^2r^2 - (\cos kr)/kr]\,Y_{10}\ ,\\ \phi_0{}^m(k\pi_u) &= A_{11}j_1(kr)Y_{11} = A_{11}[(\sin k'r)/k'^2r^2 - (\cos k'r)/k'r]\,Y_{11}\ ;\end{aligned} \tag{27}$$

and for $r>r_c$,

$$\begin{aligned}\phi_0{}^m(k\sigma_u) &= B_{10}[F_1(kr)+\tan\delta_{10}G_1(kr)]\,(kr)^{-1}Y_{10}\ ,\\ \phi_0{}^m(k\pi_u) &= B_{11}[F_1(kr)+\tan\delta_{11}G_1(kr)]\,(kr)^{-1}Y_{11}\ .\end{aligned} \tag{28}$$

This procedure was carried out for the two values of the core radius in order to get an idea of the variation in the quantities of interest with r_c. As we expected from the results given in I, the values of computed properties were relatively insensitive to the choice of r_c so long as it is in the range one would guess from the core electron density or other similar physical criteria. Having obtained the model wave functions, we orthogonalized them to the known Hartree-Fock wave functions of the ${}^2\Sigma_g^+$ core of N_2^+. The continuum wave functions so obtained were then multiplied by all the orbitals of the N_2^+ core and the products antisymmetrized.

The same procedure was carried out for the Rydberg series converging to the ${}^2\Pi_u$ state of N_2^+. Here, however, the lack of experimental data on the quantum defects limited our calculation to the $k\sigma_g$ wave only.

Let us now examine the calculation of the differential and total cross section with our approximate wave functions. The quantity of paramount importance is the transition dipole matrix element $d(lmm_qm_I)$ defined in (24). In calculating $d(lmm_qm_I)$, we assume the validity of the Born-Oppenheimer approximation and the slow variation of the integral over the electronic coordinates with the internuclear distance. This allows us to separate $d(lmm_qm_I)$ into a product of an electronic and a nuclear integral. The integral over the nuclear coordinate leads to the well known Franck-Condon factor which has been determined theoretically or experimentally[5] by a number of other workers. The electronic integral can be calculated as follows:

$$d(lmm_qm_I) \cong R_N\Big[\sum_j \int d\vec{r}\,\Psi_{qlm}^{e*}(\vec{r}_1\ldots\vec{r}_N)r_jY_{1m''}(\hat{r}_j')\Psi_I^{e}(\vec{r}_1\ldots\vec{r}_N)\Big]_{m''=m+m_q-m_I}\ , \tag{29}$$

where R_N is the Franck-Condon factor and $\Psi_I{}^e$ and $\Psi_q{}^e$ are the initial and final state total electronic wave functions at $R=R_e$. The integral over $d\vec{r}$ can be performed in standard fashion to yield

$$\begin{aligned}R_N^{-1}d(lmm_qm_I) &\cong \mathfrak{C}_{\text{core}}\Big[\int d\vec{r}_j\,\psi^*_{qlm}(\vec{r}_j)r_jY_{1m''}(\hat{r}_j')\varphi_I(\vec{r}_j)\Big]_{m''=m+m_q-m_I}\ ;\\ \mathfrak{C}_{\text{core}} &= \int d\vec{r}_1\ldots d\vec{r}_{N-1}\varphi_1{}^{F*}(\vec{r}_1)\varphi_1{}^{I}(\vec{r}_1)\ldots\varphi_{N-1}{}^{F*}(\vec{r}_{N-1})\varphi_{N-1}{}^{I}(\vec{r}_{N-1})\ .\end{aligned} \tag{30}$$

$\mathfrak{C}_{\text{core}}$ is the overlap integral between the core orbitals which are not involved in the transition. Thus we get

$$d(lmm_qm_I) \cong R_N\mathfrak{C}_{\text{core}}\Big[\int d\vec{r}_j\,\psi^*_{qlm}r_jY_{1m''}(\hat{r}_j')\varphi_I\Big]_{m''=m+m_q-m_I}\ , \tag{31}$$

where ψ_{qlm} is the pseudofunction orthogonalized to the occupied core orbitals of N_2^+ in the qth channel. All the integrals relevant to the calculation of $d(lmm_qm_I)$ were computed numerically by using either the trapezoidal rule or Simpson's method on the IBM 7094 computer at the University of Chicago. When the integrals have been obtained, it is a simple matter to get the differential cross section to any channel q from Eq. 26. For the ${}^2\Sigma_g^+$ channel of N_2^+ we get

$$\sigma({}^2\Sigma_g^+) = (4\pi^2e^2\nu/9c)\{|d_{10}|^2+2|d_{11}|^2+P_2(\cos\theta)[4|d_{10}|^2+12\,\mathrm{Re}(d_{10}d_{11}^*)+14|d_{11}|^2]/5\}$$

$$= (4\pi^2 e^2 \nu/15c)\{|d_{10}|^2 + |d_{11}|^2 - 2\,\mathrm{Re}(d_{10}d_{11}^*) + [2|d_{10}|^2 + 6\,\mathrm{Re}(d_{10}d_{11}^*) + 7|d_{11}|^2]\cos^2\theta\} \;.$$

We have used the abbreviated notation $d_{lm} = d(lmm_q m_I)$, since both m_q and m_I are zero for this case. From the definition of $d(lmm_q m_I)$ we obtain

$$d_{10} = R_N \mathfrak{C}_{\mathrm{core}} \int d\vec{r}_N \psi^*_{X10} r_N Y_{10}(\hat{r}'_N)\varphi_{3\sigma g}\,, \quad d_{11} = R_N \mathfrak{C}_{\mathrm{core}} \int d\vec{r}_N \psi_{X11} r_N Y_{11}(\hat{r}'_N)\varphi_{3\sigma g}\,, \quad (X \equiv {}^2\Sigma_g^+)\,, \tag{33}$$

For the ${}^2\Pi_u$ channel we obtain

$$\sigma({}^2\Pi_u) = (4\pi^2 e^2 \nu/9c)[A({}^2\Pi_u) + B({}^2\Pi_u)P_2(\cos\theta)] = (4\pi^2 e^2 \nu/9c)[\alpha({}^2\Pi_u) + \beta({}^2\Pi_u)\cos^2\theta] \;, \tag{34a}$$

where

$$A({}^2\Pi_u) = |d_{00}|^2 + |d_{10}|^2 + |d_{1-1}|^2 + |d_{20}|^2 + |d_{2-1}|^2 + |d_{2-2}|^2\,, \tag{34b}$$

$$\begin{aligned} B({}^2\Pi_u) = (-4\pi e^2 \nu/15c)[&\tfrac{2}{3}|d_{10}|^2 + \tfrac{2}{3}|d_{1-1}|^2 + \tfrac{10}{21}|d_{20}|^2 - \tfrac{10}{21}|d_{2-1}|^2 - \tfrac{10}{21}|d_{2-2}|^2 \\ &+ (2\sqrt{5}/3)\,\mathrm{Re}(d_{00}d_{20}^*) + 2(5/3)^{1/2}\,\mathrm{Re}(d_{00}d_{2-1}^*)^2 + 2(10/3)^{1/2}\,\mathrm{Re}(d_{00}d_{2-2}^*) + 2\,\mathrm{Re}(d_{10}d_{1-1}^*) \\ &+ (10\sqrt{3}/21)\,\mathrm{Re}(d_{20}d_{2-1}^*) - (20\sqrt{6}/21)\,\mathrm{Re}(d_{20}d_{2-2}^*) - (30\sqrt{2}/21)\,\mathrm{Re}(d_{2-1}d_{2-2}^*)] \;. \end{aligned} \tag{34c}$$

The terms of α and β are most usefully given in tabular form, as the numerical coefficients of the d's. To obtain $\sigma({}^2\Pi_u)$, the sums of products from Table I must be multiplied by $4\pi^2 e^2\nu/9c$. Note that the expressions (34a–c) and Table I are general for the angular distribution of photoelectrons from a bound π_u orbital. The coefficients were evaluated independently by hand calculation, and later by a general computer program for angular distribution coefficients. Because of the center of symmetry in the molecule, d_{10}, d_{11}, and d_{1-1} vanish. However, we have left these elements in expression (34) so that it can be used for heteronuclear diatomics such as CO, as well as for N_2. As we mentioned earlier, it has only been possible to calculate the first term in the expression for the ${}^2\Pi_u$ differential and total cross section because of the paucity of experimentally determined quantum defects for this channel.

When proper account is taken of the degeneracies of the initial and final states involved in the photoionization process, the total differential cross section for a randomly oriented ensemble of N_2 molecules can be written as

$$\sigma(\Omega) = 2\sigma({}^2\Sigma_g^+) + 4\sigma({}^2\Pi_u)\,. \tag{35}$$

In Table II we give the result of our calculation of the photoionization cross sections of N_2 for each channel

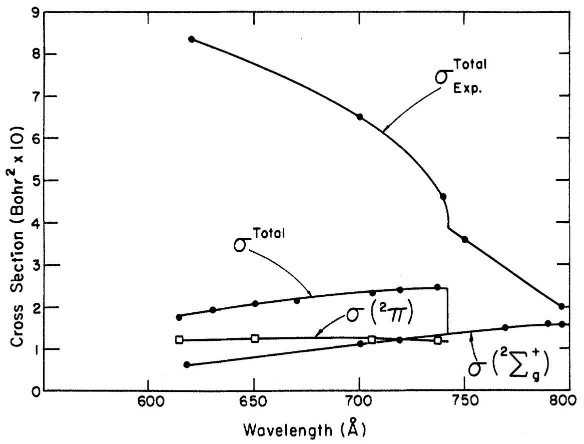

FIG. 1. Cross section for photodetachment of N_2 into ${}^2\Sigma_g^+$ and ${}^2\Pi_u$ channels, and the sum of these two; the uppermost curve is taken from the experimental data of Cook and Metzger (Ref. 2).

TABLE I. Terms of α and β for photoionization of a π_u electron.

Dipole factor	Coefficient in α	Coefficient in β
$\lvert d_{00}\rvert^2$	1	0
$\lvert d_{10}\rvert^2$	6/5	−3/5
$\lvert d_{1-1}\rvert^2$	6/5	−3/5
$\lvert d_{20}\rvert^2$	8/7	−3/7
$\lvert d_{2-1}\rvert^2$	6/7	3/7
$\lvert d_{2-2}\rvert^2$	6/7	3/7
$\mathrm{Re}(d_{00}d_{20}^*)$	$5^{-1/2}$	$-3/5^{1/2}$
$\mathrm{Re}(d_{00}d_{2-1}^*)$	$(3/5)^{1/2}$	$-3(3/5)^{1/2}$
$\mathrm{Re}(d_{00}d_{2-2}^*)$	$(6/5)^{1/2}$	$-3(6/5)^{1/2}$
$\mathrm{Re}(d_{10}d_{1-1}^*)$	3/5	−9/5
$\mathrm{Re}(d_{20}d_{2-1}^*)$	$(3/7)^{1/2}$	$-3(3^{1/2})/7$
$\mathrm{Re}(d_{20}d_{2-2}^*)$	$-2(6^{1/2})/7$	$6(6^{1/2})/7$
$\mathrm{Re}(d_{2-1}d_{2-2}^*)$	$-2(2^{1/2})/7$	$9(2^{1/2})/7$

q, obtained from (26). The calculation was carried out with both the dipole length and dipole velocity forms of the cross section in order to have a check on the numerical results and to get some indication of the error inherent in our approximation. In computing the dipole velocity form, we used the experimental energies rather than the Hartree-Fock. Where it is possible, we have listed experimental values of the calculated quantities. In Fig. 1 we have plotted the total cross section to each channel q and the experimental curve obtained by Cook and Metzger.[2] It is clear that the pseudopotential method, in its lowest-order form, gives a useful description of the photoionization cross section near threshold and becomes less accurate at energies well above threshold.

One of the most interesting aspects of molecular photoionization is the manner in which it differs from its atomic counterpart. The deviation of the molecular potential from a pure central field should manifest itself in a photoionization process in much the same way as it would in a pure scattering process. One of the most direct ways this can be demonstrated theoretically is to calculate the ratio α/β as given by Eq. 25. Comparison of theoretical and experimental values of α/β naturally places stricter demands on both theory and experiment than does the comparison of the values of total photoionization cross section. For

TABLE II. Cross sections for the photoionization of electrons from N_2.

Energy of photoionized (a.u.)	Wavelength (Å)	Length (a.u.)	Channel	total[a] σ_q	total σ_q (experimental)
5×10^{-5}	796	5	$^2\Sigma_g^+$	0.1594 (0.1147)	0.200
5×10^{-3}	789	5	$^2\Sigma_g^+$	0.1599 (0.1187)	0.225
5×10^{-3}	789	7	$^2\Sigma_g^+$	0.1477 (0.1098)	0.225
4×10^{-2}	769	5	$^2\Sigma_g^+$	0.1482 (0.1382)	0.297
4×10^{-2}	769	7	$^2\Sigma_g^+$	0.1389 (0.1068)	0.297
0.076	700	5	$^2\Sigma_g^+$	0.1109 (0.0940)	
0.1653	618	5	$^2\Sigma_g^+$	0.0612 (0.0601)	
0.1653	618	7	$^2\Sigma_g^+$	0.0799 (0.0719)	
5×10^{-3}	737	5	$^2\Pi_u$	0.1172 (0.1045)	
5×10^{-3}	737	7	$^2\Pi_u$	0.1215 (0.0933)	
2×10^{-3}	719	5	$^2\Pi_u$	0.1204 (0.1009)	
2×10^{-2}	719	7	$^2\Pi_u$	0.1132 (0.0860)	
3.125×10^{-2}	706	5	$^2\Pi_u$	0.1228 (0.0979)	
0.088	650	5	$^2\Pi_u$	0.126 (0.0817)	
0.125	614	5	$^2\Pi_u$	0.1222 (0.0701)	

[a] Numbers in parentheses refer to the calculation using the dipole-velocity form of transition matrix element; the numbers without parentheses are based on the dipole-length form.

the ${}^2\Sigma_g^+$ channel of N_2^+, we have from Eq. 32,

$$\alpha/\beta = [\,|d_{10}|^2 + |d_{11}|^2 - 2\,\mathrm{Re}(d_{10}d_{11}^*)\,]/[2\,|d_{10}|^2 + 6\,\mathrm{Re}(d_{10}d_{11}^*) + 7\,|d_{11}|^2]\ , \tag{36}$$

provided we assume that the outgoing waves are pure $p\sigma$ and $p\pi$ waves. If N_2 were truly spherically symmetric, d_{10} and d_{11} would be equal, and the ratio α/β would be zero. A nonzero value of α/β (for ionization of a σ_g electron) is a direct measure of the amount of l spoiling in the molecule. By defining

$$d_{lm} = |d_{lm}|\exp(i\delta_{lm}) \tag{37}$$

the ratio α/β becomes

$$\frac{\alpha}{\beta} = \frac{|d_{10}|^2 + |d_{11}|^2 - 2\,|d_{10}||d_{11}|\cos(\delta_{10} - \delta_{11})}{2\,|d_{10}|^2 + 7\,|d_{11}|^2 + 6\,|d_{10}||d_{11}|\cos(\delta_{10} - \delta_{11})}\ . \tag{38}$$

From this expression we find that α/β reaches its maximum when

$$\cos(\delta_{10} - \delta_{11}) = -1, \quad \text{and } |d_{11}|\,/\,|d_{10}| = \tfrac{1}{2}\ . \tag{39}$$

Substituting these values into 38, we obtain

$$(\alpha/\beta)_{\max} = 3\ . \tag{40}$$

In Table III we list the results of our computation of α/β for a number of values of k of the outgoing electron. The magnitude of α/β indicates that the nonspherical character of N_2^+ is about halfway between the central field limit and the limit defined by (39). The recent results of Berkowitz, Ehrhardt, and Tekaat[5] on the angular distribution of electrons photoionized from N_2 show a ratio of α/β somewhat larger than three. The experiments were carried out with the helium 585 Å line as an excitation source, so that the photoionized electrons carried about 6 eV of kinetic energy. There are two possible explanations, in terms of shortcomings of the theory, for the discrepancy between theory and experiment, aside from any basic deficiency in the one-electron pseudopotential model. It may be that at energies 6 eV above threshold, there are significant contributions to the partial cross section from states with quantum numbers $l \neq 1$, or that even 6 eV above threshold, long-lived autoionizing states have to be taken into account before any

TABLE III. The ratio of α/β as a function of energy for the process $N_2({}^1\Sigma_g^+) + h\nu \rightarrow N_2^+({}^2\Sigma_g^+) + e$.

Energy of photoionized electron (a.u.)	Well length (a.u.)	α/β[a]
5×10^{-5}	5	1.39 (1.25)
5×10^{-3}	5	1.61 (1.38)
5×10^{-3}	7	1.50 (1.26)
4×10^{-2}	5	1.80 (2.01)
4×10^{-2}	7	1.83 (1.50)
0.076	5	1.45 0.855
0.1653	5	(1.17) 1.17
0.1653	7	(1.36)

[a] Numbers in parentheses refer to the calculation using the dipole-velocity form of transition matrix element; the others are based on the dipole length form.

meaningful comparison with experiment can be made. Certainly if any intermediate state were involved in the transition and the autoionizing lifetime were larger than the rotational relaxation time, the ratio of α/β would go up. However, at the energies which these workers used in there experiments, autoionization is highly improbable. It is difficult to estimate the contribution of waves with $l \geqq 3$ to the photoionization cross section. Calculations of the photoionization H_2 indicate[18] that they should be approximately an order of magnitude smaller than the $l = 1$ term. At present, we have no definitive explanation for the difference between theoretical and experimental angular distributions. The fact that the experimental α/β value is greater than 3 can only be attributed to higher partial-wave contributions or to an underestimate of the experimental uncertainties. The lower α/β values derived from the microscopic theory may also reflect inadequacies of the one-electron pseudopotential model as we have used it. In the range of angles covered by the experiments the ratio

$$[{}^2\Sigma_g^+(0°)/{}^2\Sigma_g^+(40°)]_{\max} = 1.12 ,$$

while the actual ratio obtained by Ehrhardt, Berkowitz, and Tekaat was about 1.05. The reported experimental uncertainty is 15%. Thus if the error bars were just a little bit larger, the phenomenological theory and experiment would be consistent. At this stage we feel that it would be very helpful if the experiment were carried out with the neon resonance line at 743 Å, in order to compare experimental and theoretical values for α/β in a region for which only the $p\sigma$ and $p\pi$ waves are likely to be very important.

APPENDIX

We wish to make a few remarks concerning the systematic improvement of our model wave functions. The Lippman-Schwinger integral equation for our one-electron pseudofunction can be written as

$$\phi_{qlm}^- = \phi_0^m + G^-(E - i\epsilon)(V + V_R - V_m)\phi_{qlm}^- \tag{A1}$$

where

$$V_R \phi_{qlm}^- = -\sum_c \varphi_c(r)\langle \varphi_c | V - V_m | \phi_{qlm}^- \rangle , \tag{A2}$$

$$G^- = -2 \sum_{l,m} Y_{lm}^*(\hat{r}')Y_{lm}(\hat{r}) \exp(-i\delta_{lm}{}^0)[R_{lm}(k_q r)H_{lm}^-(k_q r')\mathcal{H}(r'-r) + R_{lm}(k_q r')H^-(k_q r)\mathcal{H}(r-r')] , \tag{A3}$$

and $\mathcal{H}(r)$ is the Heaviside step function, and the following limiting conditions are satisfied:

$$\lim_{r\to\infty} R_{lm}(k_q r) = k_q{}^{-1/2} r^{-1} \sin(\zeta_{ql} + \delta_{lm}{}^0) , \tag{A4}$$

$$\lim_{r\to\infty} H_{lm}^-(k_q r) = k_q{}^{-1/2} r^{-1} \exp(-i\zeta_{ql} - i\delta_{lm}{}^0) , \tag{A5}$$

and
$$\lim_{r\to\infty} \phi_0^m = \lim_{r\to\infty} 2i \exp(-i\delta_{lm}{}^0) Y_{lm}(\hat{r}) R_{lm}(k_q r) . \tag{A6}$$

Substituting (A2)–(A6) into (A1) we obtain

$$\lim_{r\to\infty} \phi_{qlm}^- = 2ik_q{}^{-1/2} r^{-1} \exp(-i\delta_{lm}{}^0) Y_{lm}(\hat{r}) \sin(\zeta_{ql} + \delta_{lm}{}^0) - 2k_q{}^{-1/2} r^{-1} \sum_\lambda [Y_{\lambda m}(\hat{r}) \exp(-i\delta_{\lambda m}{}^0) \times \exp(-i\zeta_{q\lambda} - i\delta_{\lambda m}{}^0) A_{\lambda m}{}^{lm}] , \tag{A7}$$

where
$$A_{\lambda m}{}^{lm} = \int R_{\lambda m}(k_q r) Y_{\lambda m}^*(\hat{r})[V + V_R - V_m]\phi_{qlm}^- d\vec{r} . \tag{A8}$$

We have dropped the summation over m', since the axial symmetry of $(V + V_R - V_M)$ requires that $m = m'$. Thus

$$\lim_{r\to\infty} \phi_{qlm}^- = k_q{}^{-1/2} r^{-1} Y_{lm}(\hat{r})[\exp(i\zeta_{ql}) - \exp(-2i\delta_{lm}{}^0)\exp(-i\zeta_{ql})]$$

$$- 2k_q^{-1/2} r^{-1} \sum_\lambda [A_{\lambda m}^{\;lm} Y_{\lambda m}(\hat{r}) \exp(- 2i\delta_{\lambda m}^{\;0}) \exp(- i\zeta_{q\lambda})] \,. \qquad \text{(A9)}$$

If we define

$$S_{l\lambda}^{\dagger} = \exp(- 2i\delta_{\lambda m}^{\;0})\, (\delta_{l\lambda} + 2A_{\lambda m}^{\;lm}) \,, \qquad \text{(A10)}$$

we can easily see that Eqs. (9) and (A9) are equivalent.

The above equation for ϕ_{qlm}^{-} can be solved by the standard iterative technique. By working within the pseudopotential formalism the convergence should be rapid and only a first iteration necessary. One may also project each ϕ_{qlm}^{-} on to the spherical harmonics to get a set of coupled equations in the single variable r. Temkin and Vasavada[19] have used such a procedure to calculate the phase shifts for elastic scattering of electrons from H_2^+ with excellent success. Only a few partial waves contributed appreciably to the cross section and the convergence was thus rapid. Working within the pseudopotential formalism as we do should lead to at least as rapidly a convergent expansion as that of Temkin and Vasavada, and thus should prove an excellent means of solving the integral equation. However, it should be emphasized again that in most instances one does not have to resort to such complicated calculations. Properly chosen model potentials and good bound-state wave functions are often enough to produce quite accurate results.

ACKNOWLEDGMENT

We would like to thank John Tully for his stimulating comments.

[†] Supported by the National Science Foundation, Grant No. GP-5535.

[*] Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

[1] G. L. Weissler, J. A. R. Sampson, M. Ogawa, and G. R. Cook, J. Opt. Soc. Am. 49, 338 (1959).

[2] G. R. Cook and P. H. Metzger, J. Chem. Phys. 41, 321 (1963).

[3] A. J. Blake and J. H. Carver, J. Chem. Phys. 47, 1038 (1967).

[4] Y. Tanaka, R. E. Huffman, and J. C. Larrabee, J. Quant. Spectry. Radiative Transfer 2, 451 (1962).

[5] J. Berkowitz, H. Ehrhardt, and T. Tekaat, Z. Physik 200, 69 (1967).

[6] R. E. Worley and F. A. Jenkins, Phys. Rev. 54, 305 (1938).

[7] P. K. Carroll and K. Yoshino, J. Chem. Phys. 47, 3073 (1967).

[8] R. E. Worley, Phys. Rev. 64, 207 (1943).

[9] H. Lefebvre-Brion and C. M. Moser, J. Chem. Phys. 43, 1394 (1965).

[10] V. H. Dibeler, R. M. Reese, and M. Krauss, J. Chem. Phys. 42, 2045 (1965).

[11] R. S. Berry, J. Chem. Phys. 45, 1228 (1966).

[12] J. Berkowitz and W. Chupka, private communication.

[13] J. Tully, R. S. Berry, and B. J. Dalton, Phys. Rev. 176, 95 (1968).

[14] J. Cooper and R. N. Zare, J. Chem. Phys. 48, 942 (1968).

[15] G. Breit and H. Bethe, Phys. Rev. 93, 888 (1954).

[16] M. Weinberg, R. S. Berry, and J. Tully, J. Chem. Phys. 49, 122 (1968).

[17] M. E. Rose, Elementary Theory of Angular Momentum (John Wiley & Sons, Inc., New York, 1957).

[18] M. R. Flannery and U. Öpik, Proc. Phys. Soc. (London) 86, 491 (1965).

[19] A. Temkin and K. V. Vasavada, Phys. Rev. 160, 109 (1967).