

Angular Distributions of Photoelectrons from H_2 : Effects of Rotational Autoionization^{*†}

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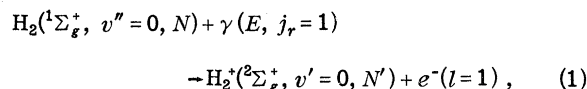
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Fano's theory of photoabsorption by H_2 near the ionization threshold is extended to yield photoelectron angular distributions above as well as between the ionization thresholds for alternative rotational states of the H_2^+ ion. In accordance with recent measurements, the angular distribution of direct photoionization is quite different depending on whether or not the ionization is accompanied by a rotational transition. In the autoionization range between rotational thresholds the angular distribution oscillates along each Rydberg line of the rotational autoionization spectrum, resulting in Beutler-Fano resonance profiles which depend strongly on angle of observation. The results are compared with available experimental data. Angular distributions provide very sensitive tests of the theory. The calculation may serve as a basis for extensions to electronic and vibrational autoionization processes.

I. INTRODUCTION

Increasing emphasis is being placed on energy analysis of molecular photoelectrons ejected into small solid angles.¹ The corresponding differential cross sections contain information which should make them sensitive probes of molecular dynamics. For example, Niehaus and Ruf^{1(a)} have recently shown that molecular photoelectron angular distributions are strongly dependent on the rotational state of the residual ion. Carlson^{1(b)} has observed energy dependences in the angular distributions of molecular photoelectrons due to the influence of autoionization on the photoelectric emission process. The theory needed to understand these effects is only just beginning to emerge.²

Here are reported and discussed the theoretical cross sections for the process



differential in the direction and energy of the photoelectron, averaged over the initial orientation of the H_2 , and integrated over the final orientation of the H_2^+ . The angular distributions are predicted to be quite different for transitions with $N'=N$ and $N' \neq N$ in accordance with the measurements of Niehaus and Ruf.^{1(a)} In addition, it is found that the angular distribution varies sharply across rotational autoionization profiles. In other words, photoelectron spectra of the autoionization peaks are expected to depend strongly on the angle of observation.

A preliminary report of the calculation has been given elsewhere.³ The calculation extends Fano's work (here referred to as FH) on photoabsorption in H_2 .⁴ The differential cross section is formulated in terms of the angular-momentum transfer theory of angular correlations, developed in the preceding

paper⁵ (here referred to as FD). In the remainder of this introductory section the analysis of reaction (1) will be outlined in the context of FH and FD. In Secs. II and III the detailed calculation is given, and in Sec. IV the explicit results are given. The calculation depends on four interaction parameters: the real dipole matrix elements d_σ and d_π for photoabsorption to $\Lambda=0$ and $\Lambda=1$, and the quantum defects μ_σ and μ_π of the Rydberg series $np\sigma$ and $np\pi$. In Sec. V it is indicated how these parameters may be determined by fitting the results to experiment.

In the calculation great effort is devoted to the detailed investigation of the various aspects of the theory. This enables us, within the relatively simple framework of the rotational problem, to focus on those basic concepts and methods that will be essential for the extension of the theory to the complex phenomena of electronic and vibrational autoionization, which are emerging as dominant features of low-energy atomic and molecular physics.

Before we proceed, one aspect of reaction (1) deserves special emphasis, namely, the photoelectron orbital angular momentum. Owing to effects of centrifugal barriers, as discussed in FH, the electron is ejected predominantly as a p wave ($l=1$), with some small f -wave ($l=3$) component. As we shall outline in Sec. IV, the angular distributions for reaction (1) with $N \neq N'$ are particularly sensitive even to small admixtures of f waves, and in fact the data of Niehaus and Ruf^{1(a)} indicate that these angular distributions do deviate from the pure p -wave values. However, in order to emphasize the main features of the photoionization process, we consider here, as in FH, the single value $l=1$ only; the extension to include f waves is straightforward, but will be postponed to a subsequent report.

Similarly, we keep $v''=v'=0$, but the theory may be extended to include vibrational interactions as

well.⁶ Only the dipole interaction with the incident light is treated ($j_r=1$), with wave number E and linear polarization along the laboratory z axis. As shown in Sec. IV, the results for unpolarized light are given by a well-known transformation of the results for linearly polarized light. Because of the weakness of the spin-rotation interaction in H_2^+ ,⁷ it is found sufficient to keep the electron spins coupled into a singlet.⁸

Accordingly, the balance of angular momentum is represented in terms of the total angular momentum

$$\vec{J} = \vec{N} + \vec{j}_r = \vec{N}' + \vec{I}, \quad (2)$$

or also in terms of the angular momentum transferred to molecular rotation

$$\vec{j}_t = \vec{N}' - \vec{N} = \vec{j}_r - \vec{I}. \quad (3)$$

From (2) or (3), together with the fact that N and N' must be of the same parity for a homonuclear diatomic molecule in a Σ state, the selection rule on N' is $N' = N$ and $N' = N \pm 2$. The corresponding values of J are $J = (N, N \pm 1)$ and $J = N \pm 1$. From (3), however, the magnitude of the angular momentum transfer is always less than or equal to 2, and processes with $N' = N \pm 2$ are consistent with the single value $j_t = 2$.

For a given initial rotational state there are then three rotational thresholds for reaction (1) given by

$$I_{N'} = I_0 - N(N+1) B_{H_2} + N'(N'+1) B_{H_2^+}, \quad (4)$$

where⁹ $I_0 = 124418.4 \text{ cm}^{-1}$ and the rotational constants B depend slightly on N and N' . To these thresholds there correspond three groups of photoelectrons with energy

$$\epsilon_{N'} (\text{a. u.}) = \frac{1}{2} k_{N'}^2 = -1/2\nu_{N'}^2, \quad (5)$$

where the energy parameters $k_{N'}$ and $\nu_{N'}$ are defined in terms of $I_{N'}$, the wave number E of the incident light, and the Rydberg constant R , through the relation

$$E = I_{N'} + R k_{N'}^2. \quad (6)$$

In the example of reaction (1) with $N=2$, consider the photoelectron in the $N'=4$ channel (and hence with $J=3$), but with $\epsilon_4 < 0$, i. e., such that the electron is bound. The electron can exchange energy with the ion core and transfer to the $N'=2$ channel (albeit at constant $J=3$). If the electron's energy is above I_2 , the electron is no longer bound and can escape to infinity. This process is rotationally induced autoionization. The crucial point is that the total angular momentum is conserved in rotational autoionization. [For example, an electron originally in the $N'=4$ channel ($J=3$) can never transfer into the $N'=0$ channel, for which $J=1$.]

In general for a given N there are two spectral regions for which autoionization is possible: (a)

for photon energies between I_{N-2} and I_N electrons in the closed channel $N' = N$, with $J = N - 1$, autoionize into the open channel $N' = N - 2$; and (b) for photon energies between I_N and I_{N+2} electrons in the closed channel $N' = N + 2$, with $J = N + 1$, autoionize into the open channel $N' = N$. Below I_{N-2} all channels are closed and the spectral region is discrete. Above, I_{N-2} lies the open continuum; all channels are open and only direct photoionization is possible. These four spectral regions are illustrated in Fig. 1 for $N=2$. The vertical arrows denote autoionization.

The amplitude for photoionization into the channel N' will be expressed in terms of the dimensionless S -matrix element $(N'l|S(J)|Nj_r)$. This matrix element is obtained in Sec. II by extending the calculation of FH, from $N=0$ to arbitrary N . The integrated cross section for reaction (1), proportional to a sum of *incoherent* contributions of the amplitudes $(N'l|S(J)|Nj_r)$, is given by¹⁰

$$\sigma^{N \rightarrow N'} = (1/4\pi) [E^2(2N+1)]^{-1} \sum_J (2J+1) |(N'l|S(J)|Nj_r)|^2. \quad (7)$$

The amplitudes $(N'l|S(J)|Nj_r)$ superpose *coherently* in the differential cross section, to give an expression complicated by interference terms. However, it is shown in FD that the differential cross section resolves into a sum of *incoherent* contributions corresponding to the alternative values of j_t which contribute to the process. Each contribution is proportional to the squared modulus of a new amplitude, defined in terms of $(N'l|S(J)|Nj_r)$ through the relation [Eq. (9) of FD, i. e., (FD9)]

$$(N'l|\bar{S}(j_t)|Nj_r) = \sum_J (-1)^{N-J-1} (2J+1) \times \left\{ \begin{matrix} l & j_r & j_t \\ N & N' & J \end{matrix} \right\} (N'l|S(J)|Nj_r). \quad (8)$$

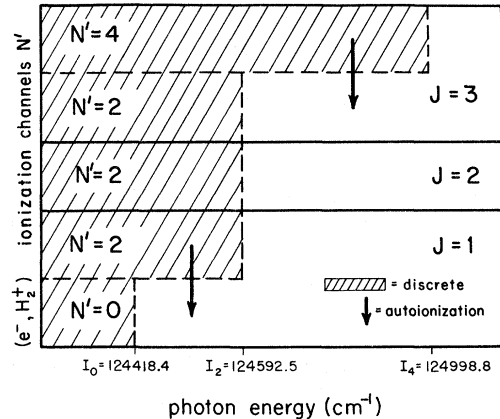


FIG. 1. Schematic representation of the spectral regions for reaction (1), with $N=2$.

Explicit expressions will be obtained for these amplitudes in Sec. III, for each spectral region and channel N' .

The differential cross section is given by, from (FD14),

$$\frac{d\sigma^{N-N'}}{d\Omega} = \frac{3}{4\pi} [E^2(2N+1)]^{-1} \times \sum_{j_t=0}^2 |(N', l=1 | \bar{S}(j_t) | N, j_r=1)|^2 \Theta(j_t; \theta), \quad (9)$$

where the angular dependence is given by the factors [cf. (FD16)]

$$\Theta(0; \theta) = (1/12\pi) [1 + 2P_2(\cos\theta)] = (1/4\pi) \cos^2\theta,$$

$$\Theta(1; \theta) = (3/12\pi) [1 - P_2(\cos\theta)] = (3/8\pi) (1 - \cos^2\theta),$$

$$\Theta(2; \theta) = (5/12\pi) [1 + \frac{1}{5}P_2(\cos\theta)] = (3/8\pi) (1 + \frac{1}{5}\cos^2\theta); \quad (10)$$

θ is the angle between the axes of linear polarization and the direction of the photoelectron.

The angular distribution law for reaction (1) is seen from (9) to have the general form $1 + \beta P_2(\cos\theta)$. It is to be emphasized that this law is a general result for dipole ionization, based on Yang's theorems,¹¹ subject only to the restrictions that the target is initially unpolarized and that no polarization analysis is performed on the residual ion. In particular it makes no difference whether the target is an atom or a molecule.

The asymmetry β is in general a weighted average of the β values given in (10), viz., $\beta = 2, -1, \frac{1}{5}$ for $j_t = 0, 1, 2$. However, when $N' = N \pm 2$, we have $\beta = \frac{1}{5}$, since only $j_t = 2$ can occur. Alternatively, processes with $N' = N$, we shall see, are dominated by the $j_t = 0$ contribution, for which $\beta = 2$. Thus, large differences between asymmetry parameters for process $N \neq N$ and $N = N'$ are seen to arise owing to alternative dominant values of j_t .

In Sec. IV A explicit expressions are given for the open continuum differential cross sections. The cross section for reaction (1) summed over all channels N' is also given; it is equivalent to the results obtained by a fixed-nuclei approximation,¹² and specifically to the result of Tully, Berry, and Dalton.^{2(c)} We compare our predicted open-continuum asymmetry parameters with measured values and with other calculations. The agreement is good.

In Sec. IV B the integrated cross section is given for rotational autoionization between I_{N-2} and I_N , into the channel $N' = N - 2(\beta^{N'-N-2} = \frac{1}{5})$. Also given is the expression for the energy-averaged integrated cross section, which pertains to measurements that do not resolve the resonance profile.

In Sec. IV C is given the differential cross section for rotational autoionization between I_N and I_{N+2} , into the channel $N' = N$. Both the integrated cross

section and the asymmetry parameter undergo sharp variations with energy, and thus the Beutler-Fano profile of the integrated cross section is predicted to show a strong angular dependence. Finally, expressions are obtained for the energy-averaged integrated cross section and asymmetry parameter.

II. MATRIX ELEMENTS ($N'l|S(J)|Nj_r$)

The matrix elements ($N'l|S(J)|Nj_r$) represent rotationally invariant amplitudes for ionization to proceed with total angular momentum J . Accordingly, we will obtain these matrix elements by expanding the photoionization dipole matrix element of reaction (1) into rotationally invariant amplitudes, with alternative values of J . FH provides the basis for the expansion procedure.

A. Expansion of Dipole Matrix Element

The dipole matrix element for reaction (1) may be written as ($E, N'm_{N'}, lm|z|Nm_N$). We expand this amplitude into amplitudes for ionization to final states of alternative values of J to give

$$(E, N'm_{N'}, lm|z|Nm_N) = \sum_J (N'm_{N'}, lm|Jm_N) (E, NlJm_N|z|Nm_N); \quad (11)$$

the first factor on the right-hand side is a Wigner coefficient. The amplitude ($E, N'lJm_N|z|Nm_N$) can be decomposed into products of two separate factors pertaining, respectively, to the photon absorption proper and to the subsequent final-state interactions of the electron-ion core system.

A feature of this separation is that the integration to obtain the dipole matrix element extends only over the region of space occupied by the ground-state electron density. In this region of space, well within the region A of FH, the electronic motion is strongly coupled to the internuclear axis and thus the dipole moment is diagonal in the molecular-frame quantum number $\Lambda = |\vec{J} \cdot \hat{z}'| \hbar^{-1}$ [\hat{z}' is the unit vector along the internuclear axis, the z axis of the body-frame (primed) coordinate system]; Hund's coupling case b applies. The corresponding dipole matrix elements are written as ($\Lambda Jm_N|z|Nm_N$), and only two values of Λ occur: $0(\sigma)$ and $1(\pi)$. (In FH this matrix element was called simply D_Λ since one dealt only with $J=1$ and $N=m_N=0$.) In the language of molecular spectroscopy, the matrix elements ($\Lambda Jm_N|z|Nm_N$) pertain to a transition between states $1s\sigma$ and $n p\Lambda$ both of which belong to Hund's case b.

Whereas the dipole matrix elements ($\Lambda Jm_N|z|Nm_N$) pertain to the body frame of reference, the complete matrix elements ($E, N'lJm_N|z|Nm_N$) are defined in the laboratory frame. Thus they depend on the connection between the two frames, namely, on the l uncoupling

process that accompanies the separation of the electron from the ion, as well as on the final-state interaction. This dependence is represented, here as in FH, by a set of coefficients $A_{\Lambda N'}^{(J)}$; these are the coefficients of the expansion of the state $|E, N' l J m_N\rangle$ into body-frame states $|\Lambda J m_N\rangle$ [see (FH20)]. Thus we write

$$(E, N' l J m_N | z | N m_N) = \sum_{\Lambda} (A^{(J)})_{N' \Lambda} (\Lambda J m_N | z | N m_N). \quad (12)$$

In the following we discuss the $(\Lambda J m_N | z | N m_N)$ and the coefficients $A^{(J)}$ separately. Note, however, that the coefficients $A^{(J)}$ vary rapidly as functions of the energy E in the autoionization region, whereas the matrix elements $(\Lambda J m_N | z | N m_N)$ vary slowly; in fact this slow variation will be disregarded altogether in this paper throughout its spectral range of interest, i. e., within several thousand cm^{-1} of the $N' = 0$ ionization threshold.

B. Body-Frame Amplitudes $(\Lambda J m_N | z | N m_N)$: Photoabsorption

In the analysis of the $(\Lambda J m_N | z | N m_N)$ we want to separate out all geometrical dependence from the purely dynamical factors which pertain to the body frame. To this end the matrix element will be reduced to separate integrals over the molecular orientation \hat{R} and over the electronic coordinates \vec{r}'_1 and \vec{r}'_2 in the body frame.

The electric dipole operator is written in the laboratory frame as

$$z \equiv z_1 + z_2 = \left(\frac{4}{3}\pi\right)^{1/2} [r_1 Y_{10}(\hat{r}_1) + r_2 Y_{10}(\hat{r}_2)], \quad (13)$$

where the notation $\hat{r} \equiv (\theta, \phi)$ is used. Transformation to the molecular frame gives

$$z = \left(\frac{4}{3}\pi\right)^{1/2} \sum_{\lambda=-1}^1 \left(\sum_{i=1,2} r_i Y_{1\lambda}(\hat{r}'_i) \right) D_{\lambda 0}^{(1)}(\hat{R}), \quad (14)$$

where $D(\hat{R})$ is the usual symmetric top eigenfunction.¹³

The initial-state wave function has the form

$$(\vec{r}'_1 \vec{r}'_2 \hat{R} | N m_N) = \left(\frac{2N+1}{4\pi}\right)^{1/2} \psi_{i,\Sigma}(\vec{r}'_1 \vec{r}'_2) D_{0 m_N}^{(N)}(\hat{R}) \quad (15)$$

and parity $(-1)^N$. The subscript Σ denotes the electronic portion of (15) as an eigenfunction of Λ with eigenvalue 0. For electric dipole interactions, the initial and final states are of opposite parity. The final-state wave function of parity $(-1)^{N+1}$ is

$$\begin{aligned} (\Lambda J m_N | \vec{r}'_1 \vec{r}'_2 \hat{R}) &= \left(\frac{2J+1}{8\pi(1+\delta_{\Lambda 0})}\right)^{1/2} [\psi_{f,\Lambda}^{\dagger}(\vec{r}'_1 \vec{r}'_2) D_{\Lambda m_N}^{(J)\dagger}(\hat{R}) \\ &+ (-1)^{\delta_{JN}} \psi_{f,-\Lambda}^{\dagger}(\vec{r}'_1 \vec{r}'_2) D_{-\Lambda m_N}^{(J)\dagger}(\hat{R})]. \quad (16) \end{aligned}$$

We see that the final-state wave function vanishes for $\Lambda = 0$ with $J = N$, i. e., Σ - Σ transitions are forbidden when $J = N$. This is a direct consequence

of parity conservation. The continuum final-state electronic wave functions $\psi_{f,\Lambda}(\vec{r}'_1 \vec{r}'_2)$ are taken to be normalized per unit energy range.

The electronic portions of the wave functions (15) and (16) are represented in the molecular frame as $\psi(\vec{r}'_1 \vec{r}'_2)$. The properties of these functions relevant here are the following: (a) They are eigenfunction of Λ ; and (b) their expansion for large values of r_1 (or r_2) coincides with the electronic part of (FH13). Hence the $\psi(\vec{r}'_1 \vec{r}'_2)$ are eigenfunctions of the photoelectron's orbital momentum l only for large r_1 or large r_2 .

The dipole matrix element can be written as

$$\begin{aligned} (\Lambda J m_N | z | N m_N) &= \int \int \int d\hat{R} d\vec{r}'_1 d\vec{r}'_2 \\ &\times (\Lambda J m_N | \vec{r}'_1 \vec{r}'_2 \hat{R}) z(\vec{r}'_1 \vec{r}'_2 \hat{R} | N m_N). \quad (17) \end{aligned}$$

Using Eqs. (14)–(16) we may carry out the integration over molecular orientation \hat{R} . The result is

$$(\Lambda J m_N | z | N m_N) = d_{\Lambda} \tilde{U}_{\Lambda N}^{(J)}(J m_N | N m_N 10), \quad (18)$$

where

$$\begin{aligned} d_{\Lambda} &= \left(\frac{4}{3}\pi\right)^{1/2} \int \int d\vec{r}'_1 d\vec{r}'_2 \\ &\times \psi_{f,\Lambda}^{\dagger}(\vec{r}'_1 \vec{r}'_2) \left[\sum_{i=1,2} r_i Y_{1\Lambda}(\hat{r}'_i) \right] \psi_{i,\Sigma}(\vec{r}'_1 \vec{r}'_2) \quad (19) \end{aligned}$$

is the (real) dipole matrix element for excitation into the $np\Lambda$ Rydberg levels of H_2 , and

$$\tilde{U}_{\Lambda N}^{(J)} = (-1)^{J-N-\Lambda} (2 - \delta_{\Lambda 0})^{1/2} (1 - \Lambda, J\Lambda | N 0) \quad (20)$$

is an element of a transformation matrix equivalent to that introduced in FH for l uncoupling, and given by (FH7). In (20) the tilde denotes transposition. A factor $(-1)^N$, included in (20), was omitted in FH where $N = 0$. While not explicitly indicated, actual evaluation of (17), and hence (19), must include integration over the internuclear distance for the $v'' \rightarrow v'$ vibrational transition of interest, which is the $0 \rightarrow 0$ transition here. (The reader is referred to Ref. 6 for details of the generalization of these results to arbitrary v'' and v' .)

The d_{Λ} given by (19) contain the fundamental dynamical information about the photon-absorption process. In this paper we treat the d_{Λ} as parameters on which the final results depend, as was done in FH for the D_{Λ} . The d_{Λ} have been determined by Herzberg and Jungen by fitting the results of FH to the high-resolution photoabsorption spectrum of H_2 .^{14(a)} Alternatively they might be calculated from first principles,^{14(b)} but this will not be considered here.

C. Coefficients $A_{\Lambda N'}^{(J)}$: Final-State Interaction

The $A_{\Lambda N'}^{(J)}$ are determined by fitting boundary conditions applied to the final-state wave function at $r = \infty$. In particular, the radial part of the wave function is normalized per unit energy range with

the incoming-wave boundary conditions appropriate to detection of outgoing electrons in a specified channel. Application of the incoming-wave boundary conditions requires the coefficient of the outgoing wave $e^{i(\mu_{N'} + \nu_{N'})}$ to vanish for $N \neq N'$ and the phase $\varphi_{N=N'}$ to vanish, and will be denoted by a minus (-) sign next to the J , $A^{(J-)}$. Two cases arise depending on the spectral region: Either all channels are open, for a given J , or one of two channels is closed (see Fig. 1).

If all channels for a given J are open, the $A_{\Lambda N}^{(J)}$ can be taken from (FH23), i. e.,¹⁵

$$A_{\Lambda N}^{(oJ-)} = e^{i\pi\mu_{\Lambda}} \tilde{U}_{\Lambda N}^{(J)}, \quad (21)$$

In (21), μ_{Λ} is the quantum defect of the $np\Lambda$ Rydberg levels of H_2 , and the superscript o denotes that this result applies to photoionization in the open continuum. The quantum defects μ_{Λ} are taken to be constant over the spectral range of interest to us,¹⁶ and they have been determined, as were the d_{Λ} , by fitting the results of FH to experiment.^{14(a)} Accordingly, the $A^{(oJ-)}$ do not depend on the photon energy E , in this case.

In the autoionization regions, only one of two channels is open, if $J = N + 1$ or $J = N - 1$, namely the channel with $N' = J - 1$. For this case, the boundary condition on the closed (unobserved) channel is that its wave-function component goes to zero exponentially as $r \rightarrow \infty$. Owing to this condition, the coefficient $A^{(J-)}$ for $N' = J - 1$ is not energy independent, but oscillates as a function of the spectral distance ν_{J+1} from the I_{J+1} threshold of the closed channel. Following FH, we express the $A^{(J-)}$ by means of a subsidiary parameter, namely, the phase shift $\Delta_{J-1}(\nu_{J+1})$ for elastic scattering of a free electron with $l = 1$ by a molecular ion with $N' = J - 1$ in a state of total angular momentum J . This phase shift is defined modulo π and is a periodic function of ν_{J+1} , with period 1. The equation (FH32) which defines $\Delta_0(\nu_2)$ is easily generalized,¹⁷ for arbitrary values of J , to

$$\frac{\sin(\pi\mu_{\sigma} - \Delta_{J-1})}{\sin(\pi\mu_{\sigma} - \Delta_{J-1})} = -\frac{J+1}{J} \frac{\sin\pi(\mu_{\sigma} + \nu_{J+1})}{\sin\pi(\mu_{\sigma} + \nu_{J+1})}. \quad (22)$$

The solution of (22) may be represented graphically by plotting $\Delta(\nu_{J+1})/\pi$ (modulo 1) as a function of ν_{J+1} (modulo 1). The resulting curve is known as a Lu-Fano plot, and is illustrated for $J = 1$ in Fig. 2(a) of FH.

The coefficients $A^{(J-)}$ for the autoionization region will be indicated by a superscript a , $A^{(aJ-)}$, and are given as functions of $\Delta(\nu_{J+1})$ by

$$A_{\Lambda, N'=J-1}^{(aJ-)} = (-1)^{\delta_{\Lambda 0}} \frac{e^{-i\Delta_{N'}}}{\tilde{U}_{\Lambda, N'=J-1}^{(J)}} \frac{\sin(\pi\mu_{1-\Lambda} - \Delta_{N'})}{\sin\pi\delta}, \quad (23a)$$

where $\delta = \mu_{\sigma} - \mu_{\sigma'}$. This result differs by the factor $e^{-i\Delta(\nu_{J+1})}$ from the corresponding result (FH40), be-

cause here we normalize the final-state wave function to incoming-wave rather than standing-wave boundary conditions.¹⁵ It is convenient to consider an alternative expression for the $A^{(aJ-)}$ in terms of the $A^{(oJ-)}$ for the open continuum, namely,

$$A_{\Lambda, N'=J-1}^{(aJ-)} = A_{\Lambda, N'=J-1}^{(oJ-)} + A_{\Lambda, N'=J+1}^{(oJ-)} \exp\{-i[\pi\nu_{J+1} + \Delta(\nu_{J+1})]\} \times \left(\frac{d\Delta(\nu_{J+1})}{d\nu_{J+1}}\right)^{1/2}, \quad (23b)$$

an expression analogous to (FH41). The contribution of the closed channel ($N' = J + 1$) to the coefficient (23b) represents the effect of autoionization and is proportional to

$$\left(\frac{d\Delta(\nu_{J+1})}{d\nu_{J+1}}\right)^{1/2} = \left(\frac{J+1}{J}\right)^{1/2} \frac{\sin[\Delta(\nu_{J+1}) - \pi\mu_{\sigma}]}{\sin\pi(\nu_{J+1} + \mu_{\sigma})}. \quad (24)$$

This formula follows from (22) and generalizes (FH39). The lifetime of the photoelectron in an autoionizing level is indeed proportional to the square of (24),¹⁸

$$\Delta t(\nu_{N'+2}) = \hbar \frac{d[\Delta(\nu_{N'+2})]}{d(\hbar\omega)} = \frac{1}{2c} \frac{R^{1/2}}{(I_{N'+2} - E)^{3/2}} \frac{d[\Delta(\nu_{N'+2})]}{d\nu_{N'+2}}. \quad (25)$$

D. Matrix Element ($N', l=1 | S(J) | N, j_r=1$)

We now proceed to obtain the desired expression for the rotationally invariant scattering matrix element ($N', l=1 | S(J) | N, j_r=1$). Combining Eqs. (11) and (18) we have

$$(E, N' m_{N'}, l m | z | N m_N) = \sum_J (N' m_N, l m | J m_N) \times \left[\sum_{\Lambda} (A^{(J-)})_{N'\Lambda}^{\dagger} d_{\Lambda} U_{\Lambda N}^{(J)} \right] (J m_N | N m_N 10). \quad (26)$$

Comparing this result with the scattering-matrix expansion given by (FD5), namely, in our notation,

$$(N' m_{N'}, l m | S | N m_N, 10) = \sum_J (N' m_{N'}, l m | J m_N) \times (N' l | S(J) | N 1) (J m_N | N m_N, 10), \quad (27)$$

we see that the matrix element ($N', l=1 | S(J) | N, j_r=1$) is proportional to the expression in brackets in (26). The proportionality factor is found by expressing the photoionization cross section σ in terms of the alternative matrix elements (26) and (27),¹⁹

$$\sigma = (2\pi)^3 e^2 E |(N' m_{N'}, l m | z | N m_N)|^2 = (3/4\pi) E^{-2} |(N' m_{N'}, l m | S | N m_N, 10)|^2, \quad (28)$$

where both matrix elements are normalized per unit energy range. The result is

$$(N', l=1 | S_i(J) | N, j_r=1) = \alpha \sum_{\Lambda} (A^{(i, J \rightarrow)})_{N' \Lambda} d_{\Lambda} \bar{U}_{\Lambda N}^{(J)}, \quad (29)$$

where $\alpha^2 = \frac{4}{3} \pi (2\pi)^3 e^2 E^3$. In (29) we have added a spectral-region index i as a subscript to $S(J)$; $i=o$ for the open continuum and $i=a$ for autoionization.

Summarizing, in this section we have used Fano's theory of photoabsorption in H_2 to obtain the expression (29) for $(N', l=1 | S(J) | N, j_r=1)$. We will now use this result, together with the expansion (8) and explicit expressions (21) and (23) for the final-state interaction coefficients $A^{(J \rightarrow)}$, to construct the matrix elements $(N', l=1 | \bar{S}(j_t) | N, j_r=1)$ for each spectral region.

III. EXPLICIT EXPRESSIONS FOR MATRIX ELEMENTS

$$(N', l=1 | \bar{S}(j_t) | N, j_r=1)$$

A. Photoionization into Open Continuum

The matrix elements of $\bar{S}(j_t)$ are given in the open continuum by Eq. (8),

$$(N' | \bar{S}_o(j_t) | N) = \sum_J (-1)^{N-J-1} (2J+1) \times \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N' & J \end{matrix} \right\} (N' | S_o(J) | N). \quad (30)$$

(Since no confusion can arise here, and below, we suppress the indices l and j_r of the matrix elements of S .) Using the expression (29), together with Eq. (21), for $(N' | S_o(J) | N)$, as well as Eq. (20), we obtain

$$(N' | \bar{S}_o(j_t) | N) = \alpha \sum_J (-1)^{N-J-1} (2J+1) \times \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N' & J \end{matrix} \right\} \sum_{\Lambda} e^{i\pi\mu_{\Lambda}} d_{\Lambda} (2 - \delta_{\Lambda 0}) \times (1 - \Lambda, J\Lambda | N'0) (N0 | 1 - \Lambda, J\Lambda). \quad (31)$$

The sum over J may be carried out analytically,²⁰ and the final result is

$$(N' | \bar{S}_o(j_t) | N) = \alpha \left(\frac{2N+1}{2j_t+1} \right)^{1/2} (j_t 0, N0 | N'0) c(j_t), \quad (32)$$

$$(N' | S_o(J) | N) = \sum_{j_t} (-1)^{N-J-1} (2j_t+1) \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N' & J \end{matrix} \right\} (N' | \bar{S}_o(j_t) | N) = \alpha \left(\frac{1}{3} \right)^{1/2} \left(\delta_{NN'} c(0) + (-1)^{N-J-1} [15(2N+1)]^{1/2} (20, N0 | N'0) \left\{ \begin{matrix} 1 & 1 & 2 \\ N & N' & J \end{matrix} \right\} c(2) \right). \quad (34)$$

B. Autoionization between I_{N-2} and I_N : $N'=N-2$

In the spectral region between I_{N-2} and I_N , only the single channel $N'=N-2$ is open, with $J=N-1$ and $j_t=2$. The matrix element of $\bar{S}(j_t)$ is

$$(N-2 | \bar{S}_a(j_t=2) | N) = (2N-1) \left\{ \begin{matrix} 1 & 1 & 2 \\ N & N-2 & N-1 \end{matrix} \right\} (N-2 | S_a(N-1) | N). \quad (35)$$

where we have introduced the amplitudes $c(j_t)$ given by

$$c(j_t) = \sum_{\Lambda} (-1)^{1-\Lambda} (2 - \delta_{\Lambda 0}) d_{\Lambda} e^{i\pi\mu_{\Lambda}} (1 - \Lambda, 1\Lambda | j_t 0). \quad (33)$$

Owing to the Wigner coefficient in (32), j_t is restricted to even values and the corresponding $c(j_t)$ are²¹

$$c(0) = \left(\frac{1}{3} \right)^{1/2} (d_{\sigma} e^{i\pi\mu_{\sigma}} + 2d_{\tau} e^{i\pi\mu_{\tau}}), \quad (33a)$$

$$c(2) = \left(\frac{2}{3} \right)^{1/2} (-d_{\sigma} e^{i\pi\mu_{\sigma}} + d_{\tau} e^{i\pi\mu_{\tau}}). \quad (33b)$$

The amplitudes $c(j_t)$ contain all of the dynamical information about the reaction (1). They may be viewed as scalar and quadrupole reaction amplitudes, for $j_t=0$ and $j_t=2$, respectively. In fact, the quadrupole amplitude $c(2)$ is seen to vanish in the united-atom limit of isotropic electron-core interaction, for which $\mu_{\sigma} = \mu_{\tau}$ and $d_{\sigma} = d_{\tau}$. It so happens that H_2 (and apparently other molecules) approaches the united-atom limit, in the sense that^{14(a)} $|c(2)| \ll |c(0)|$; this has important consequences for the photoionization spectrum (see Sec. IV A). Since $(N' | \bar{S}_o(j_t) | N)$ is proportional to a single $c(j_t)$, the amplitudes $c(j_t)$ add incoherently in direct photoionization into the open continuum. We shall see, however, that in the case of rotational autoionization the $c(j_t)$ add *coherently*, owing to the interaction between open and closed channels, which results in the autoionization. That is, we shall find matrix elements $(N' | \bar{S}_a(j_t) | N)$ which are linear combinations of $c(0)$ and $c(2)$ (see Sec. III D).

Equation (32) gives the desired explicit expression for the matrix elements $(N' | \bar{S}_o(j_t) | N)$. In the subsequent development it will be useful to have the corresponding relation for $(N' | S_o(J) | N)$. This is easily obtained by inverting the expansion (30) to give $(N' | S_o(J) | N)$ in terms of $(N' | \bar{S}_o(j_t) | N)$. The result is

We will give two different expressions for $(N-2 | \bar{S}_a(j_t=2) | N)$, obtained from the alternative forms (23) of the coefficients $A^{(a, N-1)}$. Their separate usefulness will become apparent in Sec. IV.

Using (23b) in the expression (29) for $(N-2 | S_a(N-1) | N)$ we obtain

$$(N-2 | S_a(N-1) | N) = (N-2 | S_o(N-1) | N)$$

$$+ e^{i(\pi\nu_N - \Delta_{N-2})} \left(\frac{d\Delta_{N-2}}{d\pi\nu_N} \right)^{1/2} (N | S_o(N-1) | N). \quad (36)$$

Combining (34) and (36), we obtain from (35) the result

$$(N-2 | \bar{S}_a(j_t=2) | N) = \frac{\alpha}{2N-1} \left(\frac{1}{6} \right)^{1/2} \left[3[N(N-1)]^{1/2} c(2) + e^{i(\pi\nu_N - \Delta_{N-2})} \left(\frac{d\Delta_{N-2}}{d\pi\nu_N} \right)^{1/2} [(2)^{1/2} (2N-1) c(0) - (N+1) c(2)] \right]. \quad (37)$$

Alternatively, using (23a), we obtain from (35)

$$(N-2 | \bar{S}_a(j_t=2) | N) = \alpha \left(\frac{2N-1}{5} \right)^{1/2} \frac{e^{i\Delta_{N-2}}}{\sin\pi\delta} \left[\sin(\pi\mu_\tau - \Delta_{N-2}) d_\sigma \left(\frac{N}{N-1} \right)^{1/2} + \sin(\pi\mu_\sigma - \Delta_{N-2}) d_\tau \left(\frac{N-1}{N} \right)^{1/2} \right] \\ = (-1) \alpha \left(\frac{2N+1}{5} \right)^{1/2} \frac{s}{\sin\pi\delta} \left(\frac{e^{i2[\Delta_{N-2} - \Delta_z(N-2)]} - 1}{2i} \right), \quad (38)$$

where

$$s = d_\sigma e^{i\pi\mu_\tau} \left(\frac{N}{N-1} \right)^{1/2} + d_\tau e^{i\pi\mu_\sigma} \left(\frac{N-1}{N} \right)^{1/2} \quad (39)$$

and

$$\Delta_z(N-2) = \arg s \quad (40)$$

represents the value of Δ_{N-2} for which the photoemission goes to zero. The result (38) displays a well-known property of resonance amplitudes: Its modulus describes a full circle in the complex plane every π units in the phase shift Δ_{N-2} .

C. Autoionization between I_N and I_{N+2} : $N'=N$

In the spectral region between I_N and I_{N+2} , photoionization leaving the ion with $N'=N$ is accompanied by rotational autoionization from the closed $N'=N+2$ channel ($J=N+1$). The corresponding matrix element of $\bar{S}(j_t)$ is given by

$$(N | \bar{S}_a(j_t) | N) \\ = (2N-1) \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N & N-1 \end{matrix} \right\} (N | S_o(N-1) | N) \\ - (2N+1) \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N & N \end{matrix} \right\} (N | S_o(N) | N) \\ + (2N+3) \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N & N+1 \end{matrix} \right\} (N | S_o(N+1) | N). \quad (41)$$

As for $(N-2 | \bar{S}_a(j_t=2) | N)$, we will give alternative expressions for (41), differing in the form of $(N | S_a(N+1) | N)$.

The matrix element $(N | S_a(N+1) | N)$ resolves into a sum of open-continuum matrix elements, when (23b) is used for $A^{(a_{N+1})}$, i. e.,

$$(N | S_a(N+1) | N) = (N | S_o(N+1) | N) \\ + e^{i(\pi\nu_{N+2} - \Delta_N)} \left(\frac{d\Delta_N}{d\pi\nu_{N+2}} \right)^{1/2} (N+2 | S_o(N+1) | N). \quad (42)$$

Combining this result with the expression (32) for $(N' | \bar{S}_o(j_t) | N)$, we obtain from (41)

$$(N | \bar{S}_a(j_t) | N) = (N | \bar{S}_o(j_t) | N) + e^{i(\pi\nu_{N+2} - \Delta_N)} \\ \times \left(\frac{d\Delta_N}{d\pi\nu_{N+2}} \right)^{1/2} [5(2N+3)]^{1/2} \left\{ \begin{matrix} 1 & 1 & j_t \\ N & N & N+1 \end{matrix} \right\} \\ \times (N+2 | \bar{S}_o(j_t=2) | N). \quad (43)$$

If instead we use (23a), the matrix element $(N | S_a(N+1) | N)$ is given by, analogous to (38),

$$(N | S_a(N+1) | N) \\ = \alpha \frac{e^{i\Delta_N}}{\sin\pi\sigma} [-d_\sigma \sin(\pi\mu_\tau - \Delta_N) + d_\tau \sin(\pi\mu_\sigma - \Delta_N)] \\ = (-1) \alpha \left(\frac{3}{2} \right)^{1/2} c(2)^* \frac{e^{i\pi(\mu_\sigma + \mu_\tau)}}{\sin\pi\delta} \left(\frac{e^{i2[\Delta_N - \Delta_z(N)]} - 1}{2i} \right), \quad (44a)$$

where

$$\Delta_z(N) = \pi(\mu_\sigma + \mu_\tau) - \arg c(2) \quad (44b)$$

is the value of Δ_N at which (44a) vanishes and the photoemission between I_N and I_{N+2} has a minimum. Equation (44b) is equivalent to (FH44'). A useful alternative relation for $\Delta_z(N)$ is

$$\rho = \frac{d_\sigma}{d_\tau} = \frac{\sin[\Delta_z(N) - \pi\mu_\tau]}{\sin[\Delta_z(N) - \pi\mu_\sigma]}, \quad (44c)$$

equivalent to (FH44). Using (43), together with the expression (32), we obtain from (41) the explicit results

$$(N | \bar{S}_a(0) | N) = \frac{\alpha}{3} \left(\frac{1}{2(2N+1)} \right)^{1/2} \left[N[4(2)^{1/2} c(0) + c(2) - 3(2N+3) c(2)^* \frac{e^{i\pi(\mu_\sigma + \mu_\tau)}}{\sin\pi\delta} \left(\frac{e^{i2[\Delta_N - \Delta_z(N)]} - 1}{2i} \right) \right],$$

$$(N|\bar{S}_a(1)|N) = \frac{\alpha}{6} \left(\frac{N(2N+3)^2}{(2N+1)(N+1)} \right)^{1/2} \left\{ \left[(2)^{1/2} c(0) - \left(\frac{N}{2N+3} \right) c(2) \right] + 3c(2)^* \frac{e^{i\pi(\mu_\sigma + \mu_\pi)}}{\sin\pi\delta} \left(\frac{e^{i2[\Delta_N - \Delta_\pi(N)]} - 1}{2i} \right) \right\},$$

$$(N|\bar{S}_a(2)|N) = (-1) \frac{\alpha}{6} \left(\frac{N(2N-1)(2N+3)}{5(2N+1)(N+1)} \right)^{1/2} \\ \times \left\{ \left[(2)^{1/2} c(0) + \left(\frac{5N+2}{2N-1} \right) c(2) \right] + 3c(2)^* \frac{e^{i\pi(\mu_\sigma + \mu_\pi)}}{\sin\pi\delta} \left(\frac{e^{i2[\Delta_N - \Delta_\pi(N)]} - 1}{2i} \right) \right\}. \quad (45)$$

D. Parameters $c(j_t)$

In Sec. II of FD it was shown that for systems with a body frame of reference (such as diatomic molecules) $(N'|\bar{S}(j_t)|N)$ may be expressed as the product of two factors: a geometrical factor depending on the rotational quantum numbers N and N' , and an intrinsic body-frame parameter $M(j_t)$ which is independent of rotation of the body frame. This is the essential content of the expression (32) of $(N'|\bar{S}_o(j_t)|N)$, and comparing (32) with (FD23) we obtain

$$M(j_t) = [\alpha/(2j_t + 1)^{1/2}] c(j_t).$$

The point that we wish to emphasize is that this factorization and the analysis of FD, Sec. II, applies only in the open continuum.

If autoionization can occur, the interaction between the different channels N' , responsible for the autoionization, dynamically connects molecular rotation and electron-molecule interactions in the body frame and, accordingly, the factorization is "spoiled." In fact the $(N'|\bar{S}_a(j_t)|N)$ are linear combination of the parameters $M(j_t)$ [i. e., the $c(j_t)$].

IV. RESULTS

The differential cross section for reaction (1), given by (9), has the general form

$$\frac{d\sigma_i^{N-N'}}{d\Omega} = \frac{\sigma_i^{N-N'}}{4\pi} [1 + \beta_i^{N-N'} P_2(\cos\theta)], \quad (46)$$

where i ($\equiv o, a$) indicates the spectral region. The angle θ in (46) is measured from the *axis of linear polarization* of the incident light. For unpolarized light, (46) is replaced by

$$\frac{d\sigma_i^{N-N'}}{d\Omega'} = \frac{\sigma_i^{N-N'}}{4\pi} [1 + (-\frac{1}{2} \beta_i^{N-N'}) P_2(\cos\theta')], \quad (47)$$

where θ' is measured from the *axis of incidence* of the light.²²

A. Direct Photoionization into Open Continuum

Substituting the results (32) for $(N'|\bar{S}_o(j_t)|N)$ into (9) we obtain

$$\frac{d\sigma_o^{N-N'}}{d\Omega} = \eta(E) \sum_{j_t} \left(\frac{1}{2j_t + 1} \right) \\ \times (j_t 0, N 0 | N' 0)^2 |c(j_t)|^2 \Theta(j_t; \theta), \quad (48)$$

where $\eta(E) = 3\alpha^2/4\pi E^2 = (2\pi)^3 e^2 E$. For the dipole moments d_Λ normalized per unit energy range in atomic units, we replace $\eta(E)$ by $\eta(I_0) = 4.6$ Mb over the spectral range of interest for which we assume both the dipole moments d_Λ and quantum defects μ_Λ are constant in energy.

Using the expressions (10) for the functions $\Theta(j_t; \theta)$ we obtain the following results:

$$\left. \begin{aligned} \sigma_o^{N-N-2} &= \eta(I_0) \frac{N(N-1)}{2(2N-1)(2N+1)} |c(2)|^2 \\ \beta_o^{N-N-2} &= \frac{1}{5} \end{aligned} \right\} E > I_N, \quad (49a)$$

$$\left. \begin{aligned} \sigma_o^{N-N} &= \frac{1}{3} \eta(I_0) [|c(0)|^2 + f(N) |c(2)|^2] \\ \beta_o^{N-N} &= \frac{2|c(0)|^2 + \frac{1}{5} f(N) |c(2)|^2}{|c(0)|^2 + f(N) |c(2)|^2} \\ f(N) &= \frac{N(N+1)}{(2N-1)(2N+3)} \end{aligned} \right\} E > I_{N+2}, \quad (49b)$$

$$\left. \begin{aligned} \sigma_o^{N-N+2} &= \eta(I_0) \frac{(N+1)(N+2)}{2(2N+1)(2N+3)} |c(2)|^2 \\ \beta_o^{N-N+2} &= \frac{1}{5} \end{aligned} \right\} E > I_{N+2}. \quad (49c)$$

The differential cross section (48) depends on N and N' only through the squared Wigner coefficient, which gives unity when summed over N' . Accordingly summation easily gives

$$\bar{\sigma}_o \equiv \sum_{N'} \sigma_o^{N-N'} = \frac{1}{3} \eta(I_0) (d_\sigma^2 + 2d_\pi^2), \quad \bar{\beta}_o \equiv \sum_{N'} \frac{\sigma_o^{N-N'} \beta_o^{N-N'}}{\sigma_o^{N-N'}} = \frac{2(2d_\sigma^2 + 7d_\pi^2 + 6d_\sigma d_\pi \cos\pi\delta)}{5(d_\sigma^2 + 2d_\pi^2)}, \quad E > I_{N+2} \quad (49d)$$

TABLE I. Comparison of calculated and measured open-continuum asymmetry parameters (see text for discussion).

Asymmetry parameter	Theory		Experiment		
	This work	Shaw and Berry (Ref. 23)	Niehaus and Ruf [Ref. 1(a)]	Carlson and Jonas [Ref. 1(c)]	McGowan, Vroom, and Comeaux [Ref. 1(d)]
β_o^{0-0}	2		} 1.95 ± 0.03		
β_o^{1-1}	1.87 ± 0.05				
β_o^{2-2}	1.91 ± 0.05				
$\beta_o^{N-N\pm 2}$	$\frac{1}{5}$		0.85 ± 0.14		
$\bar{\beta}_o$	1.71 ± 0.05	1.65	1.93 ± 0.03	1.75	1.6

independently of the initial rotational level N as well.

The result (49d) pertains to measurements which do not resolve (or that sum over) the final rotational state, in accordance with the general result (FD26). It is the result one obtains in a fixed-nuclei approximation,¹² and it is indeed equivalent to that obtained in the fixed nuclei calculation of Tully, Berry, and Dalton^{2(c)} [see especially Eqs. (B1)–(B3) of Ref. 2(c)].

Using the experimental values $\delta = 0.285$ and $\rho = 1 \pm 0.3$, obtained by Herzberg and Jungen,^{14(a)} we compare in Table I our predicted open-continuum asymmetry parameters with values obtained by other workers. Some caution is called for, however, since our values of δ and ρ are “threshold” values, and may differ slightly from their values several electron volts above threshold where the measurements were made.

Beginning with $\bar{\beta}_o$, we see that the agreement is quite good, with the exception of the somewhat-high value of Niehaus and Ruf. The value $\bar{\beta}_o = 1.65$ was obtained recently by Shaw and Berry²³ using an expression equivalent to (49d), together with theoretically determined values of ρ and δ .

Niehaus and Ruf have made the only measurements of asymmetry parameters for particular rotational transitions. Even though they have only partially resolved alternative transitions, as shall now be indicated, analysis of the predicted values in terms of their results has provided very valuable insights into the validity of the theory. The theoretical importance of such measurements is to be stressed.

The principal feature of both the predicted and the observed rotationally resolved asymmetry parameters is the large difference between the values for β_o^{N-N} and $\beta_o^{N-N\pm 2}$. This is due to the fact that $N \rightarrow N$ ionization proceeds primarily with $j_t = 0$, for which $\beta = 2$ [see Eq. (10)], whereas $N \rightarrow N \pm 2$ ionization proceeds entirely with $j_t = 2$, for which $\beta = \frac{1}{5}$, assuming that the photoelectron is ejected solely as a p wave ($l = 1$) (see below). Theory and experiment

are in very good agreement on the values of β_o^{N-N} . (The experiment did not resolve the $0 \rightarrow 0$ and $1 \rightarrow 1$ transitions.) More significant, however, is the very poor agreement for the $N \rightarrow N \pm 2$ transition. As we shall show in detail elsewhere, this difference can result from coupling of photoelectron p waves ($l = 1$) to f waves ($l = 3$) by the long-range quadrupole field of the molecular ion. Sichel^{2(b)} has already emphasized the possible importance of higher partial waves in molecular photoelectron angular distributions.

Here we will only sketch the preliminary analysis of the effects of f waves. The contribution of f waves to the integrated cross section is negligible, since f waves would lead to $\Delta N = 4$ transitions, which are not observed. However, if the contribution of f waves to the integrated cross section is of the order ϵ^2 ($\epsilon \ll 1$), the contribution to the asymmetry parameter, through the p - f interference term, will be of the order ϵ (no interference term could occur in the integrated cross section). Accordingly the effect of f waves on the asymmetry parameters may not be neglected solely on the basis of this absence of $\Delta N = 4$ transitions.

In fact, the effect on β_o^{N-N} (and $\bar{\beta}_o$) is expected to be negligible, of the order of a few percent; but the effect on $\beta_o^{N-N\pm 2}$ is probably substantial, perhaps amounting to as much as a factor of 2. This is because the p - f interference term occurs only for $j_t = 2$, where it is multiplied by the large statistical weight $(2j_t + 1)(2l' + 1)^{1/2}(2l + 1)^{1/2} = 5(21)^{1/2}$. The p - f term may then be comparable to the pure p -wave term in its contribution to $N \rightarrow N \pm 2$ transitions. However, it remains negligible in $N \rightarrow N$ transitions which include an additional p -wave term from $j_t = 0$; this term is an order of magnitude larger than the p -wave term from $j_t = 2$, because it follows from $\rho \sim 1$ that $|c_0| \gg |c_2|$, as noted in Sec. III A. The dominance of $j_t = 0$, for which $\beta = 2$, explains why β_o^{N-N} and $\bar{\beta}_o$ are so close to 2. It also accounts for the observation of Niehaus and Ruf [Ref. 1(a), Fig. 3, upper curve] that the combined angular distribution for the $3 \rightarrow 3$ and $2 \rightarrow 0$ transitions is essentially

the same as for the pure $N \rightarrow N$ transition.

Thus, the effect of the p - f interference term probably will account for the bulk of the deviation of the measured value of $\beta_a^{N \rightarrow N-2}$ from the "pure" p wave of $\frac{1}{5}$. On the other hand, we do not expect it to account for the difference between the predicted and measured values of β_a . Detailed verification of these points must await further experimental re-

sults. At any rate, the analysis clearly shows that the angular distribution can be a much more sensitive test of theory than the corresponding integrated cross sections.

B. Autoionization between I_{N-2} and I_N : $N' = N-2$

Using the expression (38) for $(N-2 | \bar{S}_a(j_t) | N)$ we obtain from (9)

$$\sigma_a^{N \rightarrow N-2} = \frac{1}{3} \eta(I_0) \frac{|S|^2}{\sin^2 \pi \delta} \sin^2[\Delta_{N-2} - \Delta_z(N-2)], \quad \beta_a^{N \rightarrow N-2} = \frac{1}{5}, \quad I_{N-2} < E < I_N. \quad (50)$$

Equation (50) expresses $\sigma_a^{N \rightarrow N-2}$ as a sinusoidal function of the grossly nonlinear energy scale Δ_{N-2} , with period π . When $\sigma_a^{N \rightarrow N-2}$ is mapped onto the wave-number scale, using (22), the oscillations of photoelectric current form a Rydberg series of broad asymmetric Beutler-Fano profiles, with period 1 in ν_N . The widths of the profiles are constant on the ν_N energy parameter scale, but steadily decrease with increasing wave number converging to zero at $E = I_N$.

The photoemission averaged over the resonance profile may be computed from the alternative expression (37) for $(N-2 | \bar{S}_a(j_t) | N)$. Equation (37) has the general form

$$a + e^{i(\pi\nu - \Delta)} \left(\frac{d\Delta}{d\pi\nu} \right)^{1/2} b, \quad (51)$$

where a and b represent, respectively, the constant photoelectron amplitudes in the open continuum for $N \rightarrow N-2$ and $N \rightarrow N$. As first shown by Gailitis,²⁴ and in the present context in (FH45),²⁵ it is a general feature of autoionization in Rydberg series that

the interference vanishes between amplitudes in the open and closed channels, when the cross section is averaged over the resonance profile. Thus

$$\int_{\nu}^{\nu+1} d\nu \left| a + e^{i(\pi\nu - \Delta)} \left(\frac{d\Delta}{d\pi\nu} \right)^{1/2} b \right|^2 = |a|^2 + |b|^2, \quad (52)$$

i. e., the energy-averaged cross section is given simply by the sum of open-continuum cross sections corresponding to the two interacting channels. Using the result (52) together with (37) in (9) we obtain then

$$\langle \sigma_a^{N \rightarrow N-2} \rangle_{\nu_N} = \frac{\eta(I_0)}{27(2N+1)} \times [(11N+2)d_o^2 + (5N+3)d_r^2 + (9N+1)d_o d_r \cos \pi \delta]. \quad (53)$$

C. Autoionization between I_N and I_{N+2} : $N' = N$

The differential cross section for autoionization into the channel N is given by

$$\sigma_a^{N \rightarrow N} = \frac{\eta(I_0)}{3\alpha^2(2N+1)} [|N | \bar{S}_a(0) | N \rangle|^2 + 3 |N | \bar{S}_a(1) | N \rangle|^2 + 5 |N | \bar{S}_a(2) | N \rangle|^2], \quad (54)$$

$$\beta_a^{N \rightarrow N} = \frac{2 |N | \bar{S}_a(0) | N \rangle|^2 - 3 |N | \bar{S}_a(1) | N \rangle|^2 + |N | \bar{S}_a(2) | N \rangle|^2}{|N | \bar{S}_a(0) | N \rangle|^2 + 3 |N | \bar{S}_a(1) | N \rangle|^2 + 5 |N | \bar{S}_a(2) | N \rangle|^2},$$

where the matrix elements $(N | \bar{S}_a(j_t) | N)$ are given by (43) or (45). All three values of j_t contribute here, and $\beta_a^{N \rightarrow N}$ might thus vary over the full range from -1 to 2 , for suitable values of the $|N | \bar{S}_a(j_t) | N \rangle|^2$.

From (45) we see that both $\sigma_a^{N \rightarrow N}$ and $\beta_a^{N \rightarrow N}$ are sinusoidal functions of the scattering phase shift Δ_N , with period π . The integrated cross section $\sigma_a^{N \rightarrow N}$ [and hence the denominator in the expression (54) for $\beta_a^{N \rightarrow N}$] has the general form

$$\sigma_a^{N \rightarrow N} = A + B \sin^2[\Delta_N - \Delta_z(N)], \quad (55)$$

where A and B are (non-negative) constants. The asymmetry parameter has the form

$$\beta_a^{N \rightarrow N} = \frac{C + D \sin 2[\Delta_N - \Delta_z(N)] + E \sin^2[\Delta_N - \Delta_z(N)]}{A + B \sin^2[\Delta_N - \Delta_z(N)]} \quad (56)$$

where C , D , E are independent of Δ_N (but may be negative). The second term in the numerator of (56), which oscillates between positive and negative values, is due to the interference between reaction amplitudes for different values of the total angular momentum J . This "interference term" has the effect of displacing the minimum of the asymmetry parameter from the minimum of total photoionization, which occurs at $\Delta_N = \Delta_z(N)$.

When $\sigma_a^{N \rightarrow N}(\Delta_N)$ and $\beta_a^{N \rightarrow N}(\Delta_N)$ are mapped onto the ν_{N+2} scale, their variation takes the form of Beut-

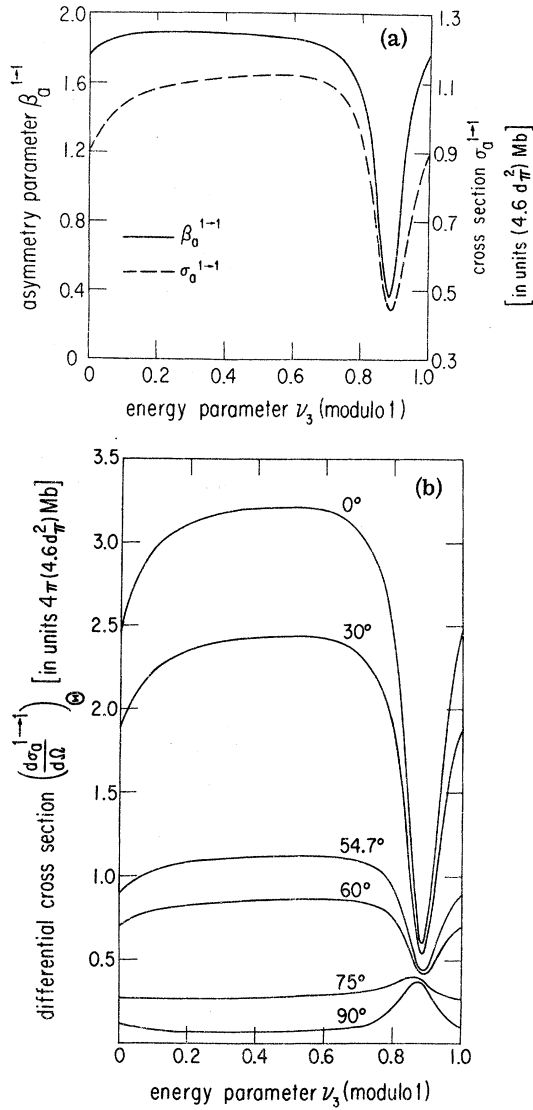


FIG. 2. (a) Resonance profiles of the integrated cross section σ_a^{1-1} and asymmetry parameter β_a^{1-1} , for one unit range of ν_3 , with $\rho=1$ and $\delta=0.285$. (b) Resonance profiles of the differential cross section $(d\sigma_a^{1-1}/d\Omega)_\theta$ for one unit range of ν_3 and several angles θ , with $\rho=1$ and $\delta=0.285$.

ler-Fano profiles. Figure 2(a) shows this mapping over one unit range of ν_{N+2} for $N=1$, using the values $\rho=1.0$ and $\delta=0.285$ obtained by Herzberg and Jungen.^{14(a)} The cycle of variation in σ_a^{1-1} and β_a^{1-1} repeats with period 1 in ν_3 , and thus forms a Rydberg series of lines. Immediately above I_1 , one unit of ν_3 corresponds to 27.4 cm^{-1} of the spectrum. This range decreases to zero as the photon wave number E approaches I_3 .

The pronounced resonance behavior of the asymmetry parameter β_a^{N-N} means that the shape of the spectrum of photoelectron current will depend

strongly on the angle of observation. That is, the line-profile index²⁶ q of the photoelectron spectrum undergoes large variations with angle. We expect this strong angular dependence of the line-profile index to be a normal feature of Beutler-Fano resonances regardless of the detailed mechanism of the phenomenon. In Fig. 2(b) this variation is illustrated for the example of Fig. 2(a).

Because the widths of the asymmetry-parameter profiles are at the limit of current resolving power, the expression for $d\sigma_a^{N-N}/d\Omega$ averaged over the resonance is particularly important. Using $(N|\bar{S}_o(j_t)|N)$ as given by (43), together with the result (52), we obtain

$$\langle \sigma_a^{N-N} \rangle_{\nu_{N+2}} = \sigma_o^{N-N} + \sigma_o^{N-N+2}, \quad (57a)$$

$$\begin{aligned} \langle \sigma_a^{N-N} \beta_a^{N-N} \rangle_{\nu_{N+2}} \\ = \sigma_o^{N-N} \beta_o^{N-N} + \sigma_o^{N-N+2} \left(\frac{1}{5} \right) \left(1 + \frac{3(2N+3)}{(2N+1)(N+1)} \right). \end{aligned} \quad (57b)$$

The result (57a) is well known,²⁷ and corresponds to (FH46). The result (57b) is new. The ratio $\langle \sigma_a^{N-N} \beta_a^{N-N} \rangle / \langle \sigma_a^{N-N} \rangle$ is the asymmetry parameter that determines the angular dependence in the photoelectron spectrum of unresolved autoionization peaks.

The term in large parentheses in (57b) approaches unity rapidly as N increases, and in the limit of large N we obtain an expression analogous to $\langle \sigma_a^{N-N} \rangle_{\nu_{N+2}}$, namely,

$$\lim_{N \rightarrow \infty} \left\langle \frac{d\sigma_a^{N-N}}{d\Omega} \right\rangle_{\nu_N} = \frac{d\sigma_o^{N-N}}{d\Omega} + \frac{d\sigma_o^{N-N+2}}{d\Omega}. \quad (58)$$

V. PARAMETER FITTING FROM EXPERIMENTAL DATA

We now indicate how and to what extent the parameters of the calculation, namely, the quantum defects and the (real) dipole matrix elements, may be determined by fitting the results to experimental data. The results for direct photoionization have the general form

$$ad_\sigma^2 + bd_\tau^2 + cd_\sigma d_\tau \cos\pi\delta = d_\tau^2 (a\rho^2 + b + c\rho \cos\pi\delta),$$

where a , b , and c are numerical coefficients. The results for autoionization depend additionally on the quantum defects, modulo 1, through the phase shifts $\Delta_N(\nu_{N+2})$ [cf. Eq. (22)]. Accordingly, to fit the theoretical to experimental results we must determine (a) the magnitudes of the dipole matrix elements; (b) the quantum defects, modulo 1; and (c) the sign²⁸ (and magnitude) of the product $\rho \cos\pi\delta$. The relative sign of d_σ and d_τ , and the integer parts of μ_σ and μ_τ , depend on phase conventions.²⁸ The product $\rho \cos\pi\delta$, however, is independent of phase conventions, and, in fact, its sign serves to fix the

TABLE II. Comparative summary of procedures for fitting theory to experiment.

Experiment	Parameter	Measurement	Resolution needed		Comments
			In energy	In intensity	
Photoelectron spectrum as a function of angle	$\rho \cos \pi \delta$ (and $ \rho $)	$\left\{ \begin{array}{l} \beta_o^{N-N} \\ \bar{\beta}_o \end{array} \right.$	$\sim 100 \text{ cm}^{-1}$	relative	must resolve $N \rightarrow N$ photoelectrons
			none	relative	no energy analysis
	$ d_\Lambda $	$\bar{\sigma}_o$	none	absolute	no energy analysis; need $\delta \text{ mod. } 1$
	μ_Λ (modulo 1)	$\Delta_z(N)$	$\sim 1 \text{ cm}^{-1}$	none	must resolve autoionization profile, on absolute energy scale; need $\delta \text{ mod. } 1$
High-resolution photoabsorption spectrum	μ_Λ (modulo 1)	Lu-Fano plot	$\sim 1 \text{ cm}^{-1}$	none	need discrete level positions
	$\rho \cos \pi \delta$ (and $ \rho $)	$\Delta_z(N)$	$\sim 1 \text{ cm}^{-1}$	none	need $\mu_\Lambda \text{ mod. } 1$; must resolve autoionization profile
	$ d_\Lambda $	$\left\{ \begin{array}{l} (\sigma_a^{N-N})_{\nu_{N+2} = \mu_\Lambda} \\ (\sigma_a^{N-N})_{\nu_{N+2} = \Delta_z/\pi} \end{array} \right.$	$\sim 1 \text{ cm}^{-1}$	absolute	need $ \rho $; must resolve autoionization profile
$\sim 1 \text{ cm}^{-1}$			absolute		

relative phase of the two terms which make up the fundamental amplitudes $c(j_\pm)$.

A possible fitting procedure, utilizing the photoelectron spectrum of reaction (1), is sketched as follows. The values of $\rho \cos \pi \delta$ and $|\rho|$ are determined from the values of $\bar{\beta}_o$ and β_o^{N-N} , using the theoretical expressions (49) for these quantities. Then, the value of $\bar{\sigma}_o$, together with $|\rho|$, allows us to determine $|d_\sigma|$ and $|d_r|$. (Only the determination of $\bar{\sigma}_o$ requires an absolute intensity measurement, and only the measurement of β_o^{N-N} requires energy analysis of the photoelectron, sufficient to resolve the rotational transition and hence of the order of a hundred cm^{-1} .) Finally, the μ_Λ are determined, modulo 1, from the positions $\Delta_z(N)$ of minimum photocurrent in the autoionization region between I_N and I_{N+2} , and the relation, based on (44c),

$$\mu_\sigma(\text{mod } 1) = \frac{1}{\pi} \left[\Delta_z(N) - \text{arccot} \left(\frac{\rho - \cos \pi \delta}{\sin \pi \delta} \right) \right]; \quad (59)$$

this expression depends only on $\rho \cos \pi \delta$ and on δ modulo 1. To determine $\Delta_z(N)$ the resonance profile must be completely resolved.

An alternative procedure, utilizing the high-resolution photoabsorption spectrum of reaction (1), is given for $N=0$ in FH and was employed by Herzberg and Jungen.^{14(a)} This procedure, for arbitrary N , is as follows. As described in detail in Sec. VII of FH, the quantum defects can be obtained, modulo 1, from the experimental determination of the plot of the phase shift Δ_N versus the en-

ergy parameter ν_{N+2} , given theoretically by Eq. (22). To construct this Lu-Fano plot, we need the positions (but not the intensities) of the discrete $n p \sigma$ and $n p \pi$ Rydberg levels, to a precision of about 1 cm^{-1} . The value $\Delta_z(N)$ is measured to obtain $\rho \cos \pi \delta$ from Eq. (44c). Then the magnitude of the dipole matrix elements can be determined from the relation

$$\begin{aligned} & [\sigma_a^{N-N}]_{(\nu_{N+2} = \mu_\Lambda)} - [\sigma_a^{N-N}]_{(\nu_{N+2} = \Delta_z/\pi)} \\ & = \eta(I_0) \frac{1}{3} \frac{2N+3}{2N+1} d_\Lambda^2, \quad (60) \end{aligned}$$

which follows from (44a) together with (22) and (7), and which is the generalization of (FH43') to arbitrary N . Use of (60) requires absolute intensity measurements on the resolved resonance profiles.

In Table II we summarize comparatively the two fitting procedures. It is clear that for determining photoionization parameters, photoelectron differential cross sections provide a very accessible alternative to the high-resolution photoabsorption spectrum. This fact, together with the high sensitivity of the angular distributions to the effects of alternative photoelectron partial waves, means that angular distributions can be expected to play an important role in our understanding of molecular dynamics.

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⁷See, e.g., A. Dalgarno, T. N. L. Patterson, and W. B. Somerville, *Proc. Roy. Soc. (London)* **A259**, 100 (1960).

⁸While in the initial state the electron spins are coupled into a singlet, it is the spin uncoupled final-state system [$H_2^+ 2\Sigma_g^+$, $e^-(l=1)$] that is detected. However, the doublet splitting of the rotational levels of the ion is negligible compared to the energy spacing of successive rotational levels (Ref. 7). Since the influence of the splitting on the photoelectron's energy will therefore generally not be resolved, the cross section for a given N' is obtained by summing the contributions from the fine-structure components $J'=N' \pm \frac{1}{2}$ of the ion and from alternative spin orientations of the photoelectron. The result coincides with the cross section obtained by treating the electron spins as remaining coupled into a singlet throughout reaction (1).

⁹See, e.g., G. Herzberg, *Phys. Rev. Letters* **23**, 1081 (1969); S. Takezawa, *J. Chem. Phys.* **52**, 5793 (1970).

¹⁰The result (7) follows from the straightforward integration of (FD14), using (FD9).

¹¹C. N. Yang, *Phys. Rev.* **74**, 764 (1948).

¹²See, e.g., (FD26) and related discussion.

¹³See, e.g., A. Messiah, *Quantum Mechanics* (Wiley, New York, 1958), p. 1074, Eq. (C.76).

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¹⁵An additional factor $\exp[-l\pi/2 + \arg\Gamma(l+1-i/k_N^*)]$ should appear in Eq. (27); however this phase factor is the same for all terms, since we consider only the single value $l=1$, and can accordingly be omitted.

¹⁶For a discussion of the energy dependence of the quantum defects see A. F. Starace, paper presented at meeting of Optical Society of America, Ottawa, 1971 (unpublished); also C. M. Lee (unpublished).

¹⁷Fano represented the transformation $U^{(J)}$ by a coordinate rotation through an angle α [c.f. (FH7)]; in (FH32) which is the origin of our Eq. (22) there appears a coefficient $-\tan^2\alpha$, whose value is -2 for the value $J=1$ considered in FH. The general form $U^{(J)}$ in Eq. (20) implies $\tan^2\alpha = (J+1)/J$.

¹⁸See, e.g., F. T. Smith, *Phys. Rev.* **118**, 349 (1960).

¹⁹For the dipole expression in Eq. (28) see, e.g., H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), Eqs. (59.5) and (69.5); for the S-matrix expression see FD, Ref. 8; and, e.g., F. J. Blatt and V. Weisskopf, *Theoretical Nuclear Physics* (Wiley, New York, 1952), pp. 317-324 and 517-521.

²⁰See, e.g., M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (The Technology Press, Cambridge, Mass., 1959), Eq. 2.19.

²¹To obtain Eqs. (33a) and (33b), as well as many of the subsequent expressions, we have used algebraic relations for Wigner coefficients and 6-j symbols given, e.g., by A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U.P., Princeton, N. J., 1960), Table 2, pp. 125-127, and Table 5, pp. 130-132.

²²Equation (47) follows from elementary geometrical transformations. See, e.g., J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, Pa., 1967), p. 42.

²³G. B. Shaw and R. S. Berry (unpublished).

²⁴M. Gailitis, *Zh. Eksperim. i Teor. Fiz.* **44**, 1974 (1963) [*Sov. Phys. JETP* **17**, 1328 (1963)].

²⁵The integral of the "diagonal" terms in (52) is just $|a|^2 + |b|^2$, since, from Eq. (22), $\Delta(\nu+1) - \Delta(\nu) = \pi$. The integral over the "interference" terms may be shown to vanish by transforming the variable of integration from ν to $\tan\pi[\nu + \frac{1}{2}(\mu_\sigma + \mu_\pi)]$, using the explicit form (24) for $(d\Delta/d\nu)^{1/2}$.

²⁶U. Fano, *Phys. Rev.* **124**, 1866 (1961).

²⁷See the discussion in Sec. IV B and Ref. 25.

²⁸The phase of d_Λ is determined by the arbitrary phase normalization of the wave function $\psi_{f,\Lambda}$ in Eq. (19). Equation (FH13) relates μ_Λ to the signs of $\psi_{f,\Lambda}$ and of standard Coulomb functions so that sign reversal of $\psi_{f,\Lambda}$ results in a shift of μ_Λ by an odd integer. Therefore, the product $\rho \cos\pi\delta$ is independent of phase normalization. [The sign of $\rho = d_\sigma/d_\pi$ given by Ref. 14(a) is tied to the conventions $-1 \leq \mu_\pi \leq 0$ and $0 \leq \mu_\sigma \leq 1$.]