

# Selection rules for the photoionization of diatomic molecules

Jinchun Xie and Richard N. Zare

Department of Chemistry, Stanford University, Stanford, California 94305

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In the photoionization of the diatomic molecule  $AB$  to yield  $AB^+ + e^-$  the photoelectron may be characterized by a partial wave expansion in terms of its orbital angular momentum quantum number  $l$ . For a given value of  $l$ , conservation of angular momentum implies that transitions can only occur for  $\Delta J = l + \frac{3}{2}, l + \frac{1}{2}, \dots, -l - \frac{1}{2}, -l - \frac{3}{2}$ , where  $\Delta J = J^+ - J$  is the change (half-integer) in the total angular momentum (excluding nuclear spin) of the  $AB^+$  ion rovibronic level and the  $AB$  neutral rovibronic level. Other selection rules are  $\Delta \Omega = -\lambda + \frac{3}{2}, -\lambda + \frac{1}{2}, \dots, -\lambda - \frac{3}{2}$ , and  $\Delta M = -m_l + \frac{3}{2}, -m_l + \frac{1}{2}, \dots, -m_l - \frac{3}{2}$ . In addition, for Hund's case (a) and case (b) coupling,  $\Delta S = S^+ - S = \pm \frac{1}{2}$ ,  $\Delta \Sigma = \pm \frac{1}{2}$ , and  $\Delta \Lambda = -\lambda, -\lambda \pm 1$ . Parity selection rules have been derived for transitions connecting levels described by one of the four coupling schemes, Hund's case (a), case (b), case (c), and case (d). In particular, for a case (a)–case (a) transition,  $\Delta J - \Delta S + \Delta p + \Delta s + l = \text{odd}$ , where the symbols have their traditional spectroscopic meanings. The parity label  $p = 0, 1$  has been associated with the  $e, f$  label, from which it may be shown that  $(e/f) \leftrightarrow (e/f)$  for  $\Delta J - \frac{1}{2} + l = \text{odd}$  and  $(e/f) \leftrightarrow (f/e)$  for  $\Delta J - \frac{1}{2} + l = \text{even}$ . It also follows that  $\pm \leftrightarrow \pm$  for  $l$  odd and  $\pm \leftrightarrow \mp$  for  $l$  even. Moreover,  $\Sigma^\pm$  is connected to  $\Sigma^\pm$  in general, but  $\Sigma^\pm$  is only connected to  $\Sigma^\mp$  for  $l \geq 2$  and  $\lambda = \pm 1$  ( $\pi$  wave). For homonuclear diatomics, the additional selection rules are  $(g/u) \leftrightarrow (g/u)$  for  $l = \text{odd}$ ,  $(g/u) \leftrightarrow (u/g)$  for  $l = \text{even}$ , and  $(s/a) \leftrightarrow (s/a)$  but  $(s/a) \leftrightarrow (a/s)$ .

## I. INTRODUCTION

Bound-bound transitions in diatomic spectroscopy obey well-known selection rules, that is, relations that must hold between the quantum numbers of the upper and lower states in order for the transitions to be allowed.<sup>1</sup> Some of these selection rules are general and exact, such as the change of parity between two combining states for an electric dipole transition. Other selection rules are only approximate, such as the conservation of spin multiplicity between two combining states. The validity of these approximate selection rules depends on how well the upper and lower states of the diatomic molecule follow various idealized angular momentum coupling schemes. Nevertheless, selection rules, exact and approximate, greatly simplify the task of establishing which transitions can occur between various energy levels of a diatomic molecule.

In this paper we seek to find the selection rules of a bound-free transition in which a diatomic molecule  $AB$  undergoes the electric-dipole-allowed photoionization process  $AB + h\nu \rightarrow AB^+ + e^-$ . Let the initial state of the  $AB$  molecule be denoted by  $|nJM_p\rangle$ , where  $J$  is the rotational quantum number,  $M$  the magnetic quantum number,  $p$  the parity, and  $n$  all other quantum numbers and labels needed to specify the state. We use a similar notation for the final state of the  $AB^+$  ion, namely,  $|n^+ J^+ M^+ p^+\rangle$ . In what follows we develop expressions for the changes in the rotational quantum numbers allowed in photoionization, i.e., we find the allowed values for  $\Delta J = J^+ - J$ ,  $\Delta M = M^+ - M$ ,  $\Delta p = p^+ - p$ , etc. We first restrict our attention to those cases in which the initial state of  $AB$  and the final state of  $AB^+$  belong to Hund's case (a) coupling. Then we discuss generalizations.

Previous one-photon photoionization experiments have seldom been able to determine the rotational selection rules governing this process. There are two major causes for this failure. First, the levels of the  $AB$  molecule are normally populated in some thermal manner that prevents a single rovibronic level to be isolated for study by one-photon photoionization. Second, there is the difficulty of monitoring the population distribution of the various vibronic levels of  $AB^+$  produced in the photoionization process. Often the kinetic energy of the photoelectron is analyzed, but photoelectron spectroscopy (PES) seldom has sufficient resolution to observe individual rotational levels of the ion. An important exception is the rotationally resolved photoelectron spectrum of  $H_2$  in one-photon ionization, first observed in 1970 by Åsbrink.<sup>2</sup> This rotational resolution results from the large rotational spacings in  $H_2$  and  $H_2^+$ .

Recently, interest in rotational selection rules in photoionization has been spurred by the use of resonance-enhanced multiphoton ionization (REMPI). Here an  $n$ -photon absorption step selects a single rovibronic level of an intermediate state. This step is followed by a one-photon bound-free transition causing photoionization of the intermediate. The resulting final states of the ion can then be determined in favorable cases either by photoelectron spectroscopy<sup>3-5</sup> or by laser-induced fluorescence (LIF).<sup>6,7</sup> Particularly noteworthy is the detection of zero kinetic energy (ZEKE) photoelectrons in coincidence with the detection of the photoion.<sup>8</sup> This new technique has a resolution of about 1 meV. When applicable, LIF can provide even higher resolution ( $10^{-3}$  meV or less).

It appears that little theoretical attention has been paid to the selection rules for photoionization. Dixit and

McKoy<sup>9</sup> have derived the parity selection rule when the transition connects two Hund's case (b) states. They have also stated without derivation the selection rule when the transition connects two Hund's case (a) states. We also note that Dehmer and co-workers<sup>3</sup> presented selection rules for their photoelectron spectra in the resonance-enhanced multiphoton ionization of H<sub>2</sub>. Here the final continuum state was treated as case (d) coupling between the ion core and the photoelectron. In this paper, we derive a complete set of selection rules for photoionization when the initial state of AB and the final state of AB<sup>+</sup> belong to either case (a), case (b), case (c), or case (d). We also discuss how the selection rules may be derived for intermediate coupling cases.

## II. DERIVATION OF SELECTION RULES

In order to establish which bound-bound transitions are allowed, it is necessary to examine the transition dipole matrix element  $\langle f | \boldsymbol{\mu} | i \rangle$  and determine under what conditions this matrix element is nonvanishing.<sup>1</sup> Here  $|f\rangle$  and  $|i\rangle$  are the wave functions of the upper and lower bound states and  $\boldsymbol{\mu}$  is the electric dipole moment operator. Similarly, for a bound-free transition causing photoionization we must examine the expression

$$\langle f | \boldsymbol{\mu} | i \rangle = \langle \text{ion} | \langle \text{photoelectron} | \boldsymbol{\mu} | \text{neutral} \rangle, \quad (1)$$

where  $|\text{neutral}\rangle$  is the initial state wave function of the AB neutral, and  $|\text{ion}\rangle$  and  $|\text{photoelectron}\rangle$  are the wave functions of the final state of the AB<sup>+</sup> ion and the final state of the ejected photoelectron.

### A. Angular momentum selection rules

It is convenient at this point to suppose that the wave functions of AB and AB<sup>+</sup> follow one of three well-known angular momentum coupling schemes,<sup>1,10</sup> first introduced by Hund and later referred to as Hund's case (a), case (b), and case (c). Then the wave functions have particularly simple forms, listed in Table I, where the angular momentum quantum numbers have their usual meanings. It is also convenient to express the photoelectron wave function either in an uncoupled representation

$$|\text{photoelectron}\rangle = |l m_l\rangle |s_e m_s\rangle \quad (2a)$$

or a coupled representation

$$\begin{aligned} |\text{photoelectron}\rangle &= |j m_j\rangle \\ &= \sum_{m_l, m_s} \langle l m_l, s_e m_s | j m_j \rangle \\ &\quad \times |l m_l\rangle |s_e m_s\rangle, \end{aligned} \quad (2b)$$

TABLE I. Wave functions for the four different Hund's coupling cases.

Coupling case	Wave function
case (a)	$ n J \Omega M \Lambda \Sigma\rangle =  J \Omega M\rangle  n \Lambda\rangle  S \Sigma\rangle$
case (b)	$ n N \Lambda M_N \Lambda S M_S\rangle =  N \Lambda M_N\rangle  n \Lambda\rangle  S M_S\rangle \text{TL}$
case (c)	$ n J \Omega M\rangle =  J \Omega M\rangle  n \Omega\rangle$
case (d)	$ n N_c \Lambda_c M_{N_c} l_R m_{lR} S M_S\rangle$ $=  N_c \Lambda_c M_{N_c}\rangle  n \Lambda_c\rangle  l_R m_{lR}\rangle  S M_S\rangle$

where  $\langle l m_l, s_e m_s | j m_j \rangle$  is a Clebsch-Gordan coefficient. Here  $l$  represents the orbital angular momentum of the electron,  $s_e$  its spin angular momentum ( $s_e = \frac{1}{2}$ ), and  $m_l$  and  $m_s$  are the projections of  $l$  and  $s_e$  on the space-fixed  $Z$  axis. We denote by  $\lambda$  and  $\sigma$  the projections of  $l$  and  $s_e$  on the molecule-fixed  $z$  axis, which is taken to coincide with the internuclear axis.

The general procedure in determining the selection rules resulting from the conservation of angular momentum is to substitute in Eq. (1) the appropriate bound state wave functions from Table I for  $|\text{neutral}\rangle$  and  $|\text{ion}\rangle$  and also to substitute into Eq. (1) the coupled or uncoupled representation for  $|\text{photoelectron}\rangle$  consistent with the coupling scheme in the molecule and the ionic core. The evaluation of Eq. (1) then leads to a product of a number of Clebsch-Gordan coefficients or equivalently 3- $j$  symbols, all of which must be nonvanishing for the transition to occur. Table II collects the resulting selection rules for transitions between the three different coupling cases.

Let us illustrate how Table II was generated by working out explicitly the selection rules when AB and AB<sup>+</sup> both follow case (a) coupling. We have

$$\langle \text{ion} | = \langle n^+ J^+ \Omega^+ M^+ \Lambda^+ S^+ \Sigma^+ |, \quad (3a)$$

$$\langle \text{photoelectron} | = \langle l m_l | \langle s_e m_s |, \quad (3b)$$

and

$$|\text{neutral}\rangle = |n J \Omega M \Lambda S \Sigma\rangle. \quad (3c)$$

Substitution of Eqs. (3a), (3b), and (3c) in Eq. (1) yields  $\langle \text{ion} | \langle \text{photoelectron} | \boldsymbol{\mu} | \text{neutral} \rangle$

$$= \sum_{\lambda, \sigma, \mu} I_1(\lambda, \sigma, \mu) I_2(\lambda, \sigma, \mu) I_3(\lambda, \sigma, \mu), \quad (4)$$

TABLE II. Angular momentum selection rules for photoionization of a diatomic molecule.

Allowed transitions (final state)-(initial state)	Selection rules
all coupling cases	$\Delta J = l + \frac{1}{2}, l + \frac{1}{2}, \dots, -l - \frac{1}{2}$ $\Delta M = -m_l + \frac{1}{2}, -m_l + \frac{1}{2}, -m_l - \frac{1}{2}$ and $-m_l - \frac{1}{2}$
case (a)-case (a) case (a)-case (b) case (b)-case (a) case (b)-case (b)	$\Delta \Lambda = -\lambda + 1, -\lambda, -\lambda - 1$ $\Delta S = \pm \frac{1}{2}$ $\Delta \Sigma = \pm \frac{1}{2}$
case (a)-case (a) case (c)-case (c) case (c)-case (a) case (a)-case (c) case (c)-case (b) case (b)-case (c)	$\Delta \Omega = -\lambda + \frac{1}{2}, -\lambda + \frac{1}{2}, -\lambda - \frac{1}{2}$ and $-\lambda - \frac{1}{2}$ or $\Delta \Omega = -\omega + 1, -\omega, -\omega - 1$
case (b)-case (b) case (d)-case (d)	$\Delta N = l + 1, l, \dots, -l - 1$ $\Delta M_N = -m_l + 1, -m_l, -m_l - 1$ $\Delta M_S = \pm \frac{1}{2}$
case (b)-case (d)	$N_c = N^+$ $l - l_R = \pm 1$

where  $I_1$  effects the transformation from the laboratory-fixed to the molecule-fixed frame,

$$I_1(\lambda, \sigma, \mu) = \int \int \int [D_{\Omega^+ M^+}^{J^+ *}(\phi, \theta, \chi) D_{\lambda m_l}^{l^*}(\phi, \theta, \chi) D_{\sigma m_s}^{s_c^*}(\phi, \theta, \chi)]^* \times D_{\mu_0}^{l^*}(\phi, \theta, \chi) D_{\Omega M}^{J^*}(\phi, \theta, \chi) d\phi \sin \theta d\theta d\chi, \quad (5)$$

$I_2$  contains the angular dependence of the integral over the electronic coordinates,

$$I_2(\lambda, \sigma, \mu) = \langle \Lambda^+ S^+ \Sigma^+ | \langle l \lambda | \langle s_c \sigma | Y_{1\mu}(\theta, \chi) | \Lambda S \Sigma \rangle, \quad (6)$$

and  $I_3(\lambda, \sigma, \mu)$  is a radial integral.

The evaluation of  $I_1$  is readily carried out using standard angular momentum coupling machinery:<sup>10</sup>

$$I_1 = K \begin{pmatrix} J^+ & j & J_t \\ M^+ & m_j & -M_t \end{pmatrix} \begin{pmatrix} l & s_c & j \\ m_l & m_s & -m_j \end{pmatrix} \times \begin{pmatrix} J & 1 & J_t \\ M & \mu_0 & -M_t \end{pmatrix} \begin{pmatrix} J^+ & j & J_t \\ \Omega^+ & \omega & -\Omega_t \end{pmatrix} \times \begin{pmatrix} l & s_c & j \\ \lambda & \sigma & -\omega \end{pmatrix} \begin{pmatrix} J & 1 & J_t \\ \Omega & \mu & -\Omega_t \end{pmatrix}, \quad (7)$$

where  $K$  is a proportionality constant and  $J_t$  is the quantum number of the total angular momentum of the system, which makes the space-fixed projection  $M_t$  and the molecule-fixed projection  $\Omega_t$ . We have also introduced in Eq. (7) the quantum number of the total angular momentum of the photoelectron in the coupled representation,  $j$ , which makes the space-fixed projection  $m_j$  and the molecule-fixed projection  $\omega$ .

In order for Eq. (7) not to vanish, it is necessary that  $J^+ = J_t + j$ ,  $J_t + j - 1, \dots, |J_t - j|$  and  $J_t = J, J \pm 1$ . It follows that

$$\Delta J = J^+ - J = j + 1, j, \dots, -j - 1. \quad (8)$$

Because  $j = l \pm s_c = l \pm \frac{1}{2}$ ,

$$\Delta J = l + \frac{3}{2}, l + \frac{1}{2}, \dots, -l - \frac{3}{2}. \quad (9)$$

For the space-fixed projections of the first three 3- $j$  symbols in Eq. (7), it follows that

$$M^+ = M_t - m_j = M + \mu_0 - m_l - m_s, \quad (10)$$

so that

$$\Delta M = M^+ - M = \mu_0 - m_l - m_s. \quad (11)$$

Thus,  $\Delta M$  ranges in unit steps from  $-m_l + \frac{3}{2}$  to  $-m_l - \frac{3}{2}$ , where  $m_s$  has been replaced by its value of  $\pm \frac{1}{2}$ , and  $\mu_0$  by its value of 0,  $\pm 1$ . For the molecule-fixed projection, the last three 3- $j$  symbols in Eq. (7) show that

$$\Omega^+ = \Omega_t - \omega = \Omega + \mu - \lambda - \sigma, \quad (12)$$

so that

$$\Delta \Omega = \Omega^+ - \Omega = \mu - \lambda - \sigma. \quad (13)$$

Thus,  $\Delta \Omega$  ranges in unit steps from  $-\lambda + \frac{3}{2}$  to  $-\lambda - \frac{3}{2}$ , where  $\sigma$  has been replaced by its value of  $\pm \frac{1}{2}$  and  $\mu$  by its value of 0,  $\pm 1$ .

The  $I_2$  integral can be further divided into two parts by an approximation in which the spin part  $|S\Sigma\rangle$  can be factored from the total electronic part of the case (a) wave function  $|\Lambda S\Sigma\rangle$ . Then we have

$$I_2 = \langle \Lambda^+ | \langle l \lambda | Y_{1\mu} | \Lambda \rangle \langle S^+ \Sigma^+ | \langle s_c \sigma | S \Sigma \rangle = K' \langle \Lambda^+ | \langle l \lambda | Y_{1\mu} | \Lambda \rangle \begin{pmatrix} S^+ & s_c & S \\ \Sigma^+ & \sigma & -\Sigma \end{pmatrix}. \quad (14)$$

Thus both electronic orbital angular momentum and electron spin angular momentum are conserved. The function  $|\Lambda\rangle$  is proportional to  $\exp(-i\Lambda\phi)$ , where  $\phi$  is an azimuthal angle measured around the internuclear axis. For the integration over the azimuthal angle not to vanish,  $-\Lambda^+ - \lambda + \mu + \Lambda = 0$ . Thus,  $\Delta\Lambda = \Lambda^+ - \Lambda = \lambda + \mu$  and it follows that  $\Delta\Lambda$  ranges in integral steps from  $-\lambda + 1$  to  $-\lambda - 1$ . From the properties of the 3- $j$  symbol in Eq. (14),  $S^+ = s_c + S$ , so that

$$\Delta S = S^+ - S = \pm \frac{1}{2} \quad (15)$$

since  $s_c = \frac{1}{2}$ . It also follows that  $\Sigma^+ + \sigma - \Sigma = 0$ , so that

$$\Delta \Sigma = \Sigma^+ - \Sigma = \pm \frac{1}{2}. \quad (16)$$

This completes the derivation of angular momentum selection rules for a case (a)–case (a) transition. Note that the case (a) wave functions form a complete basis set. Therefore, the selection rules for transitions between any two diatomic states can be worked out using the above results if the initial state and final state wave functions are first expressed as linear combinations of the case (a) basis states. In a similar manner, the angular momentum selection rules for other coupling cases can be derived.

Of special interest is the situation where the initial state is a Rydberg state that is well described by Hund's case (d) coupling. Here the Rydberg electron is atomic like and is characterized by the quantum numbers  $l_R, m_{lR}$ . The ion core has the quantum numbers  $N_c, \Lambda_c, M_{Nc}$ . We denote by  $S$  the total spin of the bound state and by  $M_S$  its space-fixed projection. Suppose that the final state of the ion is described by case (b) coupling. Then the electronic dipole matrix element is proportional to

$$\langle N^+ \Lambda^+ M_N^+ | \langle \Lambda^+ | \langle S^+ M_S^+ | \langle l m_l | \langle s_c m_s | \mu | N_c \Lambda_c M_{Nc} \rangle \times | \Lambda_c \rangle | l_R m_{lR} \rangle | S M_S \rangle. \quad (17)$$

We make the additional assumption that  $\mu$  is dominated by the motion of the Rydberg electron so that the angular dependence of  $\mu$  is  $Y_{1\mu_0}(\theta_R, \phi_R)$ . Then Eq. (17) may be rewritten as proportional to

$$\langle N^+ \Lambda^+ M_N^+ | N_c \Lambda_c M_{Nc} \rangle \langle \Lambda^+ | \Lambda_c \rangle \langle S^+ M_S^+ | \langle s_c m_s | S M_S \rangle \times \langle l m_l | Y_{1\mu_0}(\theta_R, \phi_R) | l_R m_{lR} \rangle. \quad (18)$$

Examination of this expression shows that  $\Lambda^+ = \Lambda_c$ ,  $N^+ = N_c$ , and  $M_N^+ = M_{Nc}$ , i.e., the ionic core is unchanged by photoejection of the Rydberg electron, as expected. Moreover, spin conservation gives the same result as Eq. (15) while the last integral in Eq. (18) reveals that  $l - l_R = \pm 1$ , the familiar atomic selection rule. Consequently, when it is possible to select the initial state as a case (d) Rydberg state, the resulting ionic state will have the same rotational quantum numbers as the ionic core of the

Rydberg state. This can provide in principle a unique selection of the final ion state resulting from electric-dipole-allowed photoionization.

### B. Parity selection rules

Each wave function associated with an energy level may be classified as having even or odd parity according to whether it remains unchanged or changes sign or inversion of the spatial coordinates of all particles through the origin. Only states of opposite parity can be connected by an electric dipole transition, i.e., the overall parity of the electric dipole matrix element must be even. From this we derive the parity selection rules for electric-dipole-allowed photoionization.

The effect of the parity operator  $i_{sp}$  on different parts of the wave function has been worked out in detail elsewhere.<sup>10,11</sup> We present here the results we need. In particular, for a case (a) wave function

$$\begin{aligned} i_{sp}|J\Omega M\rangle &= (-1)^{J-\Omega}|J-\Omega M\rangle, \\ i_{sp}|n\Lambda\rangle &= (-1)^{\Lambda+s}|n-\Lambda\rangle, \\ i_{sp}|S\Sigma\rangle &= (-1)^{S-\Sigma}|S-\Sigma\rangle, \end{aligned} \quad (19)$$

where  $s = 0$ , except for  $\Sigma^-$  states in which case  $s = 1$ . This allows us to introduce a case (a) basis set with well-defined parity. These parity-adapted wave functions have the form

$$\begin{aligned} |n J\Omega M \Lambda S\Sigma p\rangle &= (1/\sqrt{2})[|J\Omega M\rangle|n\Lambda\rangle|S\Sigma\rangle + (-1)^p \\ &\times |J-\Omega M\rangle|n-\Lambda\rangle|S-\Sigma\rangle], \end{aligned} \quad (20a)$$

where  $p$  is the parity quantum number ( $p = 0$  or  $1$ ), and for the special case  $\Lambda = 0$ ,  $\Sigma = 0$ ,

$$|n JOM OS0 p\rangle = |JOM\rangle|n0\rangle|S0\rangle, \quad (20b)$$

where  $p = 0$ . When  $i_{sp}$  acts on the wave function shown in Eq. (20), we find that the total parity of the wave function is given by

$$P = (-1)^{J-S+s+p}. \quad (21)$$

We also need the parity of the photoelectron wave function. It is readily shown that

$$i_{sp}|lm_l\rangle = (-1)^l|lm_l\rangle \quad (22a)$$

and

$$i_{sp}|s_e m_s\rangle = |s_e m_s\rangle. \quad (22b)$$

Finally, we note that the electric dipole moment operator is an odd function of the spatial coordinates so that

$$i_{sp}\mu = -\mu. \quad (23)$$

We consider next the electric dipole moment matrix element between states of well-defined parity, using our case (a) parity-adapted wave functions:

$$\begin{aligned} \langle f|\mu|i\rangle &= \langle n^+ J^+ \Omega^+ M^+ \Lambda^+ S^+ \Sigma^+ p^+ | \\ &\times \langle lm_l | \langle s_e m_s | \mu | n J\Omega M \Lambda S\Sigma p \rangle. \end{aligned} \quad (24)$$

For this matrix element not to vanish its parity must be even. Application of Eqs. (19), (22), and (23) shows that this condition implies that

$$J^+ - S^+ + s^+ + p^+ + l + 1 + J - S + s + p = \text{even}. \quad (25a)$$

Alternatively, this condition can be expressed as

$$\begin{aligned} (J^+ - J) - (S^+ - S) + (s^+ - s) \\ + (p^+ - p) + l = \text{odd} \end{aligned} \quad (25b)$$

Equation (25) tells us whether an even partial wave or an odd partial wave is responsible for a transition with a given  $\Delta J$ ,  $\Delta S$ ,  $\Delta s$ , and  $\Delta p$ . This result agrees with the parity selection rule given in Eq. (2) of Ref. 9, as well as Eq. (13) of Raseev and Cherepkov.<sup>12</sup>

Because any wave function can be written as a linear combination of case (a) wave functions, it is possible to derive the parity selection rules for electric-dipole-allowed transitions between any two levels of a diatomic molecule. We find it useful to consider some selected transitions between levels that are well described by Hund's case (b), case (c), or case (d). We present in Table III the parity-adapted wave functions for each coupling case. We also make use of the fact that for case (c) wave functions when  $\Omega$  is half integral,

$$i_{sp}|n\Omega\rangle = (-1)^{\Omega-1/2}|n-\Omega\rangle, \quad (26)$$

TABLE III. Parity wave functions for the four different Hund's coupling cases.

Coupling case	Parity wave function	Parity
case (a) for $\Lambda = 0$ and $\Sigma = 0$	$(1/\sqrt{2})[ J\Omega M\rangle n\Lambda\rangle S\Sigma\rangle + (-1)^p J-\Omega M\rangle n-\Lambda\rangle S-\Sigma\rangle]$ $ n JOM OS0\rangle$	$(-1)^{J-S+p+s}$ above with $p = 0$
case (b) for $\Lambda = 0$	$(1/\sqrt{2})[ N\Lambda M_N\rangle n\Lambda\rangle + (-1)^p N-\Lambda M_N\rangle n-\Lambda\rangle] SM_S\rangle$ $ NOM_N\rangle n0\rangle SM_S\rangle$	$(-1)^{N+p+s}$ above with $p = 0$
case (c) for $\Omega = 0$	$(1/\sqrt{2})[ J\Omega M\rangle n\Omega\rangle + (-1)^p J-\Omega M\rangle n-\Omega\rangle]$ $ JOM\rangle n0\rangle$	$J = \text{integer},$ $(-1)^{J+p+s}$ $J = \text{half-integer},$ $(-1)^{J-1/2+p+s}$ above with $p = 0$
case (d) for $\Lambda_c = 0$	$(1/\sqrt{2})[ N_c\Lambda_c M_{Nc}\rangle n\Lambda_c\rangle + (-1)^p N_c-\Lambda_c M_{Nc}\rangle n-\Lambda_c\rangle]$ $ I_R m_{IR}\rangle SM_S\rangle$ $ N_c OM_{Nc}\rangle n0\rangle I_R m_{IR}\rangle SM_S\rangle$	$(-1)^{N_c+I_R+p+s}$ above with $p = 0$

where we adopt the convention of Kopp and Hougen<sup>13</sup> for half integers. Similarly, for half-integral  $j$  this implies that

$$i_{sp}|jm_j\rangle = (-1)^{j-1/2}|jm_j\rangle \quad (27)$$

for the photoelectron wave function when it is expressed in the coupled representation. The parity of the electric dipole moment matrix element is readily evaluated, and results are collected in Table IV. Please note that for Hund's case (c)  $s = 0$  for all states except  $0^-$ , in which case  $s = 1$ .

A key point is to relate the value of  $p$  to the two  $\Lambda$  doublets in case (a) and case (b) coupling, or the two  $\Omega$  doublets in case (c) coupling. These components may be labeled as  $e$  or  $f$  using the following definitions:<sup>14</sup>

for integral  $J$  values:

levels with parity  $P = +(-1)^J$  are  $e$  levels,

levels with parity  $P = -(-1)^J$  are  $f$  levels;

and for half-integral  $J$  values:

levels with parity  $P = +(-1)^{J-(1/2)}$  are  $e$  levels,

levels with parity  $P = -(-1)^{J-(1/2)}$  are  $f$  levels.

Thus, the  $e$  and  $f$  levels transform in the same way as the rotational levels of  $^1\Sigma^+$ ,  $^2\Sigma^+$ , and  $^1\Sigma^-$ ,  $^2\Sigma^-$ , respectively. Examination of the parity-adapted wave functions for the four different Hund's coupling cases leads to an association of the  $e$  and  $f$  labels with the different values of the good quantum numbers. The results are listed in Table V. This identification of the  $e$  and  $f$  levels with the different  $\Lambda$  doublets and  $\Omega$  doublets is extremely useful for the analysis of open-shell diatomic molecules.

It is also convenient to classify the parity of a level as simply "+" or "-." It follows from Eq. (25) that

$$\pm \leftrightarrow \pm \text{ for } l \text{ odd} \quad (28a)$$

and

$$\pm \leftrightarrow \mp \text{ for } l \text{ even.} \quad (28b)$$

Here  $l$  should be replaced by  $j - \frac{1}{2}$  when the photoelectron is described in its coupled representation. Because we can associate the  $e$  and  $f$  labels with their parities, as shown in Table

TABLE V. Relations between  $e/f$  labels and  $p + s$  values.<sup>a</sup>

Coupling case	Label	$p + s$	Quantum number relation
case (a)	$e$	0	$S$ or $S - \frac{1}{2} = \text{even}$
	$f$	1	
	$e$	1	$S$ or $S - \frac{1}{2} = \text{odd}$
	$f$	0	
case (b)	$e$	0	$i - S$ or $i - S - \frac{1}{2} = \text{odd}$
	$f$	1	
	$e$	1	$i - S$ or $i - S - \frac{1}{2} = \text{even}$
	$f$	0	
case (c)	$e$	0	
	$f$	1	
case (d)	$e$	0	$(k + i - S)$ or $(k + i - S + \frac{1}{2}) = \text{even}$
	$f$	1	
	$e$	1	$(k + i - S)$ or $(k + i - S + \frac{1}{2}) = \text{odd}$
	$f$	0	

<sup>a</sup>Here  $i$  numbers the spin multiplicity of the rotational level  $N$ . The index  $i$  runs from 1 to  $2S + 1$  and satisfies the relation  $N = J + i - S - 1$ . The index  $k$  numbers the multiplicity resulting from the Rydberg electron  $l_R$  in rotational level  $N_c$ ; it runs from 1 to  $2l_R + 1$ , and it satisfies the relations  $N_c = N + k - l_R - 1$  and  $N_c = J + i + k - S - l_R + 2$ .

V, we can also write the selection rules

$$(e/f) \leftrightarrow (e/f) \text{ for } \Delta J - \frac{1}{2} + l = \text{odd}, \quad (29a)$$

$$(e/f) \leftrightarrow (f/e) \text{ for } \Delta J - \frac{1}{2} + l = \text{even}, \quad (29b)$$

where  $\Delta J = J^+ - J$  is always half integral in photoionization.

One additional selection rule emerges when the photoionization process connects two  $\Sigma$  states in case (a) or (b). For simplicity we use the parity-adapted case (a) basis set, Eq. (20b). Then, Eq. (24) factors into an integral over the electronic coordinates times an integral over the rotational coordinates. (Note that this is not true when  $\Lambda \neq 0$ .) In particular, the electronic integral has the form

$$\langle \Lambda^+ = 0 | Y_{l-\lambda} Y_{1\mu} | \Lambda = 0 \rangle. \quad (30)$$

TABLE IV. Parity selection rules for photoionization of a diatomic molecule.

Allowed transition (final state)-(initial state)	Selection rule
case (a)-case (a)	$(J^+ - J) - (S^+ - S) + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (a)-case (b)	$[N^+ - (J - S)] + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (b)-case (a)	$[(J^+ - S^+) - N] + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (b)-case (b)	$(N^+ - N) + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (a)-case (d)	$[(J^+ - S^+) - (N_c + l_R)] + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (b)-case (d)	$[N^+ - (N_c + l_R)] + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (c)-case (c)	$(J^+ - J) + (p^+ - p) + (s^+ - s) + l = \text{odd}^a$
case (b)-case (c)	$(N^+ - J) + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (a)-case (c)	$[(J^+ - S^+) - J] + (p^+ - p) + (s^+ - s) + l = \text{odd}$
case (c)-case (b)	$(J^+ - N^+) + (p^+ - p) + (s^+ - s) + l = \text{odd}^a$
case (c)-case (a)	$[J^+ - (J + S)] + (p^+ - p) + (s^+ - s) + l = \text{odd}^a$

<sup>a</sup>Here we may also choose the coupled scheme for the photoelectron wave function because the ion core follows Hund's case (c). Then  $l$  is replaced by  $j - \frac{1}{2}$ .

Here  $\mu = 0, \pm 1$  and  $\lambda = -\mu$ . Upon applying  $i_{sp}$  to Eq. (30),  $\langle \Lambda^+ = 0 |$  contributes a phase factor  $(-1)^{s^+}$ , and  $|\Lambda = 0\rangle$  a phase factor  $(-1)^s$ . However,  $Y_{l-\lambda} Y_{1\mu}$  is generally not a parity eigenfunction but is even under the conditions that  $\lambda = -\mu = 0$  or  $\lambda = -\mu = \mp 1$  for  $l = 1$ . For Eq. (30) to be nonvanishing,  $\Delta s = s^+ - s = 0$ , i.e.,

$$\Sigma^\pm \leftrightarrow \Sigma^\pm, \quad (31a)$$

$$\Sigma^\pm \not\leftrightarrow \Sigma^\mp, \quad (31b)$$

except  $l \geq 2$  and  $\lambda = \pm 1$ .

### C. Additional selection rules for homonuclear diatomics

When the two nuclei are identical, the electronic states of the homonuclear diatomic molecule may be further classified as gerade (*g*) or ungerade (*u*), depending on whether the electronic wave function is unchanged or changes sign upon inversion of the electronic coordinates in the molecular frame. In addition, the rotational levels may be classified as symmetric (*s*) or antisymmetric (*a*) upon exchange of the nuclei. The result of introducing these additional symmetry labels is that electric-dipole-allowed photoionization has the added selection rules

$$(g/u) \leftrightarrow (g/u) \quad \text{for } l \text{ odd}, \quad (32a)$$

$$(g/u) \leftrightarrow (u/g) \quad \text{for } l \text{ even}, \quad (32b)$$

and

$$(s/a) \leftrightarrow (s/a), \quad (33a)$$

$$(s/a) \not\leftrightarrow (a/s). \quad (33b)$$

These selections are readily derived using the treatment presented in the previous section on parity selection rules by including the effects of the nuclear permutation operator on the identical nuclei, which is equivalent to the spatial inversion of all molecular coordinates followed by the spatial inversion of the nuclei.<sup>15</sup>

### III. CONCLUDING REMARKS

In this paper we have presented the selection rules for electric-dipole-allowed photoionization of a diatomic molecule when the initial state is a single rotational level. We have shown what final rotational levels of the ion can be accessed and how these levels are related to each partial wave of the photoelectron. The derivation given is general and the results of many special limiting coupling cases have been worked out. This treatment is readily extended to two-photon and higher-order photon transitions, if desired. It also applies to photodetachment of negative ions.

The selection rules are given in terms of nomenclature for diatomic molecules. However, these results can be directly generalized to linear polyatomic molecules (with  $C_{\infty v}$  or  $D_{\infty h}$  symmetry) provided that the ion state is also linear. It is also possible to extend this treatment to more complex situations, such as when the initial and final states are described by symmetric top wave functions. So far, these considerations have been restricted to photoionization where an electron with orbital angular momentum *l* and spin angular momentum  $s_e$  is ejected. Another possible extension of this work is to replace the electron by a composite particle (fragment) having both internal and orbital angular momentum. In this manner it may be possible to derive selection rules on photofragmentation, such as what states are possible when for example a linear triatomic molecule dissociates into an atom and a diatomic molecule.

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