

Rotational line strengths for the photoionization of diatomic molecules

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We derive an expression for the probability that a diatomic molecule $AB(n, v, N)$ in the electronic state n , vibrational state v , and rotational level N yields upon photoionization $AB^+(n^+, v^+, N^+)$, where we assume Hund's case (b) coupling. Our result is formally equivalent to the previous work of Buckingham, Orr, and Sichel [Phil. Trans. Roy. Soc. London, Ser. A **268**, 147 (1970)] but differs substantially in that we use spherical tensor methods, which provide insight into the photoionization dynamics in terms of the contribution of different multipole moments. The total interaction term is given by the tensor product of the electric dipole moment operator $T(1, \mu_0)$ and the multipole moment tensor $T(l, m)$ describing the photoelectron in the l th partial wave. The interaction term is further simplified into a sum of reduced multipole moments $T(k, p)$, where $k = l \pm 1$ and $p = \mu_0 + m$. For an isotropic distribution of initial states, the transition probability is given by $P(N, N^+) = \frac{1}{3} \sum_k S^k(N, N^+) |\bar{\mu}(k, q)|^2$, where the factor of $\frac{1}{3}$ arises from the use of a beam of polarized light, $S^k(N, N^+)$ is a generalized rotational line strength factor, and $|\bar{\mu}(k, q)|^2 = |\mu_{l=k+1}(k, q)|^2 + |\mu_{l=k-1}(k, q)|^2$ is the sum of the squares of reduced multipole moment matrix elements. The summation over k is restricted to even values for a $(\pm) \leftrightarrow (\pm)$ transition and to odd values for a $(\pm) \leftrightarrow (\mp)$ transition. Thus, for an unpolarized molecular sample, the integrated photoelectron intensity associated with an $N \rightarrow N^+$ transition is the incoherent sum of the multipole moments that contribute to this transition, and each such contribution is an incoherent sum over $l = k + 1$ and $l = k - 1$. If the molecular sample is polarized (aligned and/or oriented), then the expression for the $N \rightarrow N^+$ integrated photoelectron intensity becomes a coherent sum over different k values with the same l value. Moreover, if the photoelectron distribution is angle resolved, then the expression for the $N \rightarrow N^+$ transition probability is a coherent sum over l values with the same k value when the molecular sample is unpolarized and cannot be separated into incoherent parts when the molecular sample is polarized. The expression for $P(N, N^+)$ has been used to fit the results of the photoionization of H_2 and NO . In both cases, the fit obtained, which required only one or two adjustable parameters, respectively, agrees well with the experimental data. This treatment may be readily extended to photoionization of polyatomic molecules and to molecules that follow different angular momentum coupling cases.

I. INTRODUCTION

Most photoionization studies of diatomic molecules lack rotational specificity because the neutral AB molecule is thermally populated and the ionic AB^+ product or its companion e^- photoelectron is not detected with sufficient energy resolution to establish the final rotational level of AB^+ .¹ Recent experimental advances now allow the study of the photoionization process



with rotational resolution in which the rovibronic level of the AB neutral is described by the quantum numbers (v, N) and that of the ion by (v^+, N^+) . In these experiments more than one photon is absorbed to cause ionization. For example, a one-photon bound-bound transition selects a particular rovibronic level of the AB molecule, and a second photon causes a bound-free transition to ionize the molecule in the selected level. The rotational level of the resulting AB^+ ion is then determined by energy analysis of the low-energy photoelectron (LEKE spectroscopy),²⁻⁴ by detection of the zero kinetic energy photoelectron (ZEKE

spectroscopy),⁵⁻⁷ or by laser-induced fluorescence (REMPI-LIF spectroscopy).^{8,9} In this paper we derive expressions for the probability of the transition $N \rightarrow N^+$ for a fixed $v \rightarrow v^+$ photoionization process.

Expressions for rotational line strengths for one-photon bound-bound transitions in diatomic molecules are readily found in the literature.¹⁰⁻¹² The theory of rotational line strengths for two-photon transitions was first developed for Raman scattering by Placzek and Teller.¹³ Later, when two-photon absorption spectroscopy became more common through the development of high-power pulsed laser sources, Bray and Hochstrasser¹⁴ derived a general form for the two-photon rotational line strength factor. Polarization effects in two-photon spectroscopy have also been derived by McClain and Harris,¹⁵ Chen and Yeung,¹⁶ Metz *et al.*,¹⁷ and Kummel *et al.*¹⁸ Three-photon line strengths have been worked out by Halpern *et al.*¹⁹ for diatomic molecules and by Nieman²⁰ and Dixon *et al.*²¹ for polyatomic molecules. More recently, Mainos²² considered n -photon transitions for diatomic molecules, and Chiu²³ considered four-photon transitions for polyatomic mole-

TABLE I. Quantum number nomenclature.

Angular momentum	Mol. frame projection	Lab. frame projection	Description
N	Λ	M_N	Total angular momentum excluding electron spin of the neutral molecule
N^+	Λ^+	M_N^+	Total angular momentum excluding electron spin of the ionic molecule
l	λ	m	Orbital angular momentum of the photoelectron
1	μ	μ_0	Angular momentum of the "dipole" photon
k	q	p	Angular momentum of the reduced multipole moment

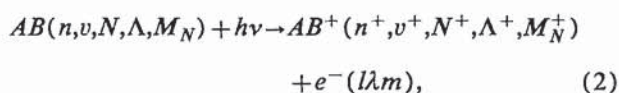
cules. The treatment presented in this paper follows closely in spirit that of Dixon *et al.*²¹

The theory of molecular photoionization has drawn extensively from that for atomic photoionization. The photoelectron angular distribution is well described,²⁴⁻²⁸ and the spin polarization of the photoelectrons has been considered.²⁹ In addition, Müller-Dethlefs³⁰ has presented rotational line strengths for ZEKE spectroscopy, and Gilbert and Child³¹ have presented a quantum defect calculation showing the importance of l mixing by the ionizing field. In these treatments, photoionization probabilities are obtained by taking the square modulus of the transition matrix element, a procedure that often yields complex expressions involving sums of products of electric dipole moment matrix elements and 3- j symbols.

In this paper we present expressions for the rotational line strengths for photoionization of diatomic molecules in which we disentangle the angular part from other terms. We assume that the interaction of the molecule with the ionizing photon is represented by the electric dipole operator and that the photoelectron is described by a partial wave $|lm\rangle$ that has an angular momentum l making a projection m on the quantization axis and λ on the internuclear axis. Thus, we ignore higher-order interactions, such as quadrupole transitions and transitions caused by the electric field of the laser beams. We formulate the interaction using irreducible spherical tensor operators. This treatment is a continuation of our study involving rotational selection rules for the photoionization of diatomic molecules.³² The primary focus of the present work is in deriving an expression for the integrated cross section for photoionization, but the results are easily extended to include photoelectron angular distributions.

II. INTENSITY DISTRIBUTION IN A ROTATIONALLY RESOLVED PHOTOELECTRON SPECTRUM

Consider the photoionization process



where the AB molecule in the vibrational level v of the electronic state n (not necessarily the ground state) makes an electric-dipole-allowed transition to the ionization continuum that yields the AB^+ molecular ion in the vibra-

tional level v^+ of the electronic state n^+ (usually the ground state). We suppose that the electronic states n and n^+ both follow Hund's case (b) coupling so that N and N^+ denote the rotational quantum numbers of AB and AB^+ , respectively. The projection of the rotational angular momentum N on the space-fixed Z axis is denoted by M_N and on the molecule-fixed z axis (the internuclear axis) by Λ , with the corresponding quantities for N^+ denoted by M_N^+ and Λ^+ . With this choice of coupling scheme, the spin of the electron is not acted upon by the electric-dipole-allowed transition. We further assume that the spin-rotation splitting is so small that individual fine-structure levels associated with $\mathbf{J}=\mathbf{N}+\mathbf{S}$ (and $\mathbf{J}^+=\mathbf{N}^++\mathbf{S}^+$) are not resolved. Table I summarizes all the quantum numbers that appear in this treatment.

A. Angle-integrated intensity for an isotropic molecular sample

The probability for the photoionization process described by Eq. (2) for a beam of polarized radiation is proportional to the square of the electric dipole moment matrix element summed over all initial and final magnetic sublevels (assuming that the initial state can be described as unoriented and unaligned). Ignoring proportionality constants, we write

$$P(l) = \sum_m \sum_{M_N, M_N^+} |\langle n^+ v^+, N^+ \Lambda^+ M_N^+ | \times \langle l\lambda m | \mu | n v, N \Lambda M_N \rangle|^2. \quad (3)$$

The electric dipole operator μ transforms under rotation as a spherical harmonic $Y_{1\mu_0}$, i.e., as a spherical tensor of rank one and projection μ_0 , where μ_0 is determined by the polarization of the electric vector associated with the ionizing radiation. Hence we replace μ by $T(1, \mu_0)$. The photoelectron eigenstate $\langle l\lambda m |$ transforms under rotation as a spherical harmonic Y_{lm}^* , and we replace it by the spherical tensor $T(l, -m)$. We then use the result for the multiplication (contraction) of the product of two spherical tensors to write¹²

$$T(l, -m) \otimes T(1, \mu_0) = \sum_{k=l-1}^{l+1} (-1)^{l-1+p} (2k+1)^{1/2} \\ \times \begin{pmatrix} l & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} T(k, p), \quad (4)$$

where the term containing six arguments in parentheses is a standard 3- j symbol, the sum over k extends from $l-1$ to $l+1$ in unit steps, and $p = -m + \mu_0$. The states of a diatomic molecule have well-defined parity. In particular, the parity for a spherical tensor of rank k is $(-1)^k$. Thus, for the electric dipole moment matrix element to have even parity, only terms with $k=l-1$ and $l+1$ are allowed, i.e., we can omit the term with $k=l$ in the sum shown in Eq. (4).

We transform the spherical tensor operator $T(k, p)$ from the laboratory to the molecular frame:¹²

$$T(k, p) = \sum_q D_{pq}^{k*}(R) T(k, q), \quad (5)$$

where $D_{pq}^{k*}(R)$ is a Wigner rotation matrix element with Euler angles represented by R . By substituting Eqs. (4) and (5) into (3) and assuming the Born–Oppenheimer separation of electronic and nuclear motions, we obtain

$$P_l(N, N^+) = \sum_m \sum_{M_N, M_N^+} \left| \sum_{k=l\pm 1} (-1)^{l-1+p} \right. \\ \times (2k+1)^{1/2} \begin{pmatrix} l & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} \\ \times \sum_q \langle N^+ \Lambda^+ M_N^+ | D_{pq}^{k*}(R) | N \Lambda M_N \rangle \\ \left. \times \langle n^+ v^+ \Lambda^+ | T(k, q) | n v \Lambda \rangle \right|^2. \quad (6)$$

In the summation over q , the first matrix element represents $D_{pq}^{k*}(R)$ evaluated between two symmetric-top wave functions,

$$|N \Lambda M_N\rangle = \left[\frac{2N+1}{8\pi^2} \right]^{1/2} D_{M_N \Lambda}^{N*}(R) \quad (7a)$$

and

$$\langle N^+ \Lambda^+ M_N^+ | = \left[\frac{2N^++1}{8\pi^2} \right]^{1/2} D_{M_N^+ \Lambda^+}^{N^+}(R). \quad (7b)$$

Hence, this term becomes proportional to the integral over the triple product of Wigner rotation matrices with the same arguments, and we find that

$$\langle N^+ \Lambda^+ M_N^+ | D_{pq}^{k*}(R) | N \Lambda M_N \rangle \\ = [(2N+1)(2N^++1)]^{1/2} \begin{pmatrix} N & k & N^+ \\ M_N & p & -M_N^+ \end{pmatrix} \\ \times \begin{pmatrix} N & k & N^+ \\ \Lambda & q & -\Lambda^+ \end{pmatrix}, \quad (8)$$

i.e., this term becomes proportional to a product of two 3- j symbols.

On the other hand, the second term appearing in the summation over q in Eq. (6) cannot be evaluated without knowledge of the electronic structure of the molecule and the molecular ion; hence, we treat this term as a parameter whose value can either be calculated from first principles or must be determined from experiment. Relating this second term to other, more familiar notations is useful:

$$\langle n^+ v^+ \Lambda^+ | T(k, q) | n v \Lambda \rangle \\ = \sum_{\lambda} (-1)^{l-1+q} (2k+1)^{1/2} \\ \times \begin{pmatrix} l & 1 & k \\ -\lambda & \mu & -q \end{pmatrix} r_{l\lambda} \exp(i\eta_{l\lambda}), \quad (9)$$

where

$$r_{l\lambda} \exp(i\eta_{l\lambda}) = \left\langle n^+ \Lambda^+ v^+ \left| \left\langle l\lambda \right| \sum_s r_s Y_{l\lambda}(\hat{r}_s) \right| n \lambda v \right\rangle \quad (10)$$

is the radial dipole moment matrix element. In Eq. (9) the dipole photon makes a projection $\mu = \lambda + q$ on the internuclear axis and $\eta_{l\lambda}$ represents the phase shift of the outgoing $l\lambda$ wave. In Eq. (10) s is an index that labels an electron whose distance from the origin is r_s .

Upon substituting these results into Eq. (6), we obtain

$$P_l(N, N^+) = \frac{1}{3} \sum_{k=l\pm 1} S^k(N, N^+) |\mu_l(k, q)|^2, \quad (11)$$

where the factor $\frac{1}{3}$ arises from the use of a polarized beam that causes photoionization (for natural excitation¹² this factor would be unity),

$$S^k(N, N^+) = (2N+1)(2N^++1) \\ \times \begin{pmatrix} N & k & N^+ \\ \Lambda & \Lambda^+ - \Lambda & -\Lambda^+ \end{pmatrix}^2 \quad (12)$$

is a *generalized rotational line strength factor*, and

$$|\mu_l(k, q)|^2 = |\langle n^+ v^+ \Lambda^+ | T(k, q) | n v \Lambda \rangle|^2 \\ = \left| \sum_{\lambda} (-1)^{l-1+q} (2k+1)^{1/2} \right. \\ \left. \times \begin{pmatrix} l & 1 & k \\ -\lambda & \mu & -q \end{pmatrix} r_{l\lambda} \exp(i\eta_{l\lambda}) \right|^2 \quad (13)$$

is the square of the reduced multipole moment matrix element. Because of the orthogonality of the 3- j symbols [see Eq. (2.32) of Ref. 12], the cross terms in Eq. (6) vanish, causing Eq. (11) to have a simple form.

Equation (11) completely disentangles the (calculable) line strength factors from the reduced multipole moment terms; it represents a major result of this paper. So far, we have obtained the photoionization probability for the $l\lambda$ partial wave. The total photoionization probability requires a sum over all possible partial waves:

$$P(N, N^+) = \sum_l P_l(N, N^+). \quad (14)$$

Actually the summation in Eq. (14) is more restricted than it might seem at first because of the parity selection rule, namely, that only a $(\pm) \leftrightarrow (\mp)$ transition is allowed for even l values and a $(\pm) \leftrightarrow (\pm)$ transition for odd l values. Thus, in Eq. (14) only the $l+1$ and $l-1$ terms contribute for each l wave and l is only even or odd:

$$P(N, N^+) = \frac{1}{3} \sum_l [S^{l-1}(N, N^+) |\mu_l(l-1, q)|^2 + S^{l+1}(N, N^+) |\mu_l(l+1, q)|^2], \quad (15)$$

where $q = \Lambda^+ - \Lambda$.

In Eq. (15), the generalized rotational line strength factor may be brought outside the quantity in square brackets by grouping terms with the same k values:

$$P(N, N^+) = \frac{1}{3} \sum_k S^k(N, N^+) |\bar{\mu}(k, q)|^2, \quad (16)$$

where

$$|\bar{\mu}(k, q)|^2 = |\mu_{k+1}(k, q)|^2 + |\mu_{k-1}(k, q)|^2. \quad (17)$$

Here the sum over k is 0, 2, 4, ... for a $(\pm) \leftrightarrow (\pm)$ transition and 1, 3, 5, ... for a $(\pm) \leftrightarrow (\mp)$ transition. When $k=0$, the last term in Eq. (17) does not exist.

Equation (16) expresses the angle-integrated photoionization probability for a $N \rightarrow N^+$ transition in terms of only two factors, the generalized rotational line strength S^k [see Eq. (12)] and the reduced multipole moment matrix element $|\bar{\mu}(k, q)|^2$ [see Eqs. (13) and (17)]. The S^k factors are readily evaluated by standard means¹² so no explicit algebraic expressions are given for them. The $|\bar{\mu}(k, q)|^2$ factors are to be determined by *ab initio* calculations or by fitting experimental data using Eq. (16). Hence, Eq. (16) is the central result of this treatment, and it is expected to be valid provided that the Born-Oppenheimer separation is a good approximation. Equation (16) is formally equivalent³³ to Eq. (20) of Buckingham, Orr, and Sichel.²⁵ Some advantages of the present derivation are that it separates the different multipole moment contributions to the transition probability $P(N, N^+)$ and indicates what terms vanish because of parity selection rules.

Equation (16) offers another advantage. It permits us to determine the minimum number of independent parameters necessary to express the different $\Delta N = N^+ - N$ transition probabilities for a given $\Delta\Lambda = \Lambda^+ - \Lambda$ photoionization process. For the photoionization from a single rotational level, the obvious appearance of the maximum value of ΔN in the spectrum directly indicates the highest value of k , i.e., the highest rank of spherical tensor moment contributing to the transition by the relation $\Delta N \leq \pm k_{\max}$. For such a transition, we need only $(k_{\max} - 1 - q)$ number of independent parameters $|\bar{\mu}(k, q)|^2$ for determining or fitting the relative rotational intensities of the spectrum. This number is less than k_{\max} because of $k \geq q (= \Lambda^+ - \Lambda)$, and the $|\bar{\mu}(k, q)|^2$ parameters need be known only up to a

normalization constant. The parity selection rule for diatomic molecules divides the $|\bar{\mu}(k, q)|^2$ parameters into two groups, those with even k for $\Delta N = \text{even}$ and those with odd k for $\Delta N = \text{odd}$. The angular momentum selection rule $\Delta N = 0, \pm 1, \dots, \pm k$ limits the $|\bar{\mu}(k, q)|^2$ parameters to contribute only to $\Delta N \leq \pm k$ transitions. This situation is similar to the case of a two-photon transition in which only two dipole moment factors μ_S^2 and μ_I^2 contribute to the relative intensities.⁸

This treatment relates the angular momentum selection rule, $\Delta N = 0, \pm 1, \dots, \pm k$, to different photoelectron partial waves l . We consider as an example where the s and d partial waves are predominantly produced from the photoionization of a diatomic molecule in a p Rydberg state. Traditionally, we will find the selection rule $\Delta N = 0, \pm 1$ for an s wave and $\Delta N = 0, \pm 1, \pm 2, \pm 3$ for a d wave. Suppose that the $\Delta N = 0$ and ± 1 transitions are much more intense than the others. Understanding the role of the d wave is difficult in this transition, but from the point of view of our treatment, the $\Delta N = 0, \pm 1$ propensity indicates the major contribution is $k=1$ so that $\mu_{l=2}(1, q) \neq 0$ whereas $\mu_{l=2}(3, q) = 0$. Therefore the propensity very clearly shows how the d waves are involved in the transition. In other words, the appearance of $\Delta N = 0$ and ± 1 does not imply that the d wave makes no contribution to the photoionization dynamics.

Equation (16) is also applicable to n -photon nonresonant ionization. In a similar manner to the one-photon process, we can replace the dipole moment operator μ^j of the j th photon by a tensor $T(1, \mu_j^i)$ and replace the photoelectron wave function by a tensor $T(l, -m)$. Therefore, we have a product of n first-rank spherical tensors with a spherical tensor of rank l . In a way similar to Eq. (4), we rewrite the product of these tensors into a sum of irreducible spherical tensors $T(k, q)$, where $k = n, n \pm 1, \dots, n \pm l$. Taking the two-photon nonresonant ionization as an example, we replace Eq. (17) with

$$|\bar{\mu}(k, q)|^2 = |\mu_{k+2}(k, q)|^2 + |\mu_k(k, q)|^2 + |\mu_{k-2}(k, q)|^2, \quad (18)$$

where

$$\begin{aligned} \mu_i(k, q) = & \sum_{\lambda} \sum_{\mu^1 \mu^2} \sum_{i, i^1} (-1)^{l-i-\lambda} [(2k+1)(2i+1)]^{1/2} \\ & \times \begin{pmatrix} 1 & 1 & i \\ \mu^1 & \mu^2 & -\mu^i \end{pmatrix} \begin{pmatrix} l & i & k \\ -\lambda & \mu^i & -q \end{pmatrix} \\ & \times r_{l\lambda\mu^1\mu^2} \exp(i\eta_{l\lambda\mu^1\mu^2}). \end{aligned} \quad (19)$$

In Eq. (19), μ^1 , μ^2 , and μ^i denote the internuclear axis projections for the first photon, the second photon, and the total angular momentum i of the two photons. In Eq. (18), only three terms with $l=k$, $k \pm 2$ appear because the parity selection rule has removed the terms with $l=k \pm 1$. For an n -photon process, similar results can be derived to those in Eqs. (18) and (19).

B. Other cases

The present treatment has greatly simplified the expression for the photoionization process by minimizing the numbers of independent parameters. For photoionization from an isotropic initial state, the angle-integrated intensity for an $N \rightarrow N^+$ transition is simply represented by an incoherent sum over the multipole moments, as shown in Eq. (16). For other cases, however, cross terms between different reduced multipole moments appear and complicate the resulting expression for $P(N, N^+)$. We consider three cases, the rotationally resolved angle-integrated photoelectron intensity distribution from an anisotropic initial state, the angle-resolved photoelectron intensity distribution from an isotropic initial state, and the angle-resolved photoelectron intensity distribution from an anisotropic initial state.

Consider first the rotationally resolved angle-integrated photoelectron intensity from an anisotropic initial state. Strictly speaking, we should use a density matrix formulation so that we can express not only the population of the different (N, M_N) sublevels of the initial state (the

diagonal elements of the ${}^N\rho_{M_N, M'_N}$ density matrix) but also the different phase relations between these levels (the off-diagonal elements of the ${}^N\rho_{M_N, M'_N}$ density matrix).^{4(c)} For simplicity, however, we limit ourselves here to situations having cylindrical symmetry, i.e., all photons are in the same pure polarization state. Then we need consider only the different populations $n(N, M_N)$ of the sublevels (N, M_N) .

An example of this situation is $(n+1)$ REMPI, where n photons bring the molecule from the ground state to an intermediate state and another photon of the same color and (pure) polarization ionizes the intermediate state. Experimentally, the relative intensity for an $N \rightarrow N^+$ transition is obtained either by probing the internal state distribution of the resulting molecular ion using LIF or by measuring the photoelectron kinetic energy distribution with sufficient resolution that individual $N \rightarrow N^+$ rotational transitions are resolved. Theoretically, the angle-integrated photoelectron intensity for an $N \rightarrow N^+$ transition is given by

$$P(N, N^+) = (2N+1)(2N^++1) \sum_{l,m} \sum_{M_N, M_N^+} \sum_{k,k'} n(N, M_N) [(2k+1)(2k'+1)]^{1/2} \begin{pmatrix} l & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} \begin{pmatrix} l & 1 & k' \\ -m & \mu_0 & -p \end{pmatrix} \\ \times \begin{pmatrix} N & k & N^+ \\ M_N & p & -M_N^+ \end{pmatrix} \begin{pmatrix} N & k' & N^+ \\ M_N & p & -M_N^+ \end{pmatrix} \begin{pmatrix} N & k & N^+ \\ \Lambda & q & -\Lambda^+ \end{pmatrix} \begin{pmatrix} N & k' & N^+ \\ \Lambda & q & -\Lambda^+ \end{pmatrix} \mu_l(k', q) \mu_l(k, q). \quad (20)$$

Here cross terms appear between the reduced multipole moments with different ranks k and k' but with the same partial wave l . The incoherent contribution from the partial waves is a consequence of the angular integration. If the photoionization process starts from an isotropic state, i.e., $n(N, M_N) = 1$, then Eq. (20) reduces to Eq. (16). For $(n+1)$ REMPI, each $n(N, M_N)$ population factor is proportional to the n -photon M_N -dependent transition probability and can be varied by choosing different transition branches or polarizations of the light source.

Next, consider the situation in which the photoelectron angular distribution is observed. The starting point is the matrix element for the ionization step

$$\langle f | \mu | i \rangle = \sum_{k=l\pm 1} (-1)^{l-1+p} (2k+1)^{1/2} \begin{pmatrix} l & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} \\ \times \langle N^+ \Lambda^+ M_N^+ | D_{pq}^* | N \Lambda M_N \rangle \mu_l(k, q) Y_{lm}(\theta_k, \phi_k), \quad (21)$$

where θ_k and ϕ_k are the spherical polar angles of the ejected photoelectron, and the $Y_{lm}(\theta_k, \phi_k)$ are spherical harmonics. The angle-resolved intensity distribution for an $N \rightarrow N^+$ rotational transition from an isotropic initial state may be written as

TABLE II. The relations between the reduced multipole moments $\mu_l(k, q)$ and the dipole moments $r_{l\lambda}$ for a $\Delta\Lambda=0$ transition.

Photoelectron partial wave	Relation ^a
<i>s</i> wave ($l=0$)	$\mu_0(1,0) = r_{0,0}$
<i>p</i> wave ($l=1$)	$\mu_1(0,0) = -\sqrt{\frac{1}{3}}r_{1,0} + 2\sqrt{\frac{1}{3}}r_{1,1}$ $\mu_1(2,0) = \sqrt{\frac{2}{3}}r_{1,0} + \sqrt{\frac{2}{3}}r_{1,1}$
<i>d</i> wave ($l=2$)	$\mu_2(1,0) = -\sqrt{\frac{2}{5}}r_{2,0} + \sqrt{\frac{6}{5}}r_{2,1}$ $\mu_2(3,0) = \sqrt{\frac{3}{5}}r_{2,0} + 2\sqrt{\frac{1}{5}}r_{2,1}$
<i>f</i> wave ($l=3$)	$\mu_3(2,0) = -\sqrt{\frac{3}{7}}r_{3,0} + 2\sqrt{\frac{2}{7}}r_{3,1}$ $\mu_3(4,0) = \sqrt{\frac{4}{7}}r_{3,0} + \sqrt{\frac{6}{7}}r_{3,1}$
<i>g</i> wave ($l=4$)	$\mu_4(3,0) = -\sqrt{\frac{4}{9}}r_{4,0} + \sqrt{\frac{6}{9}}r_{4,1}$ $\mu_4(5,0) = \sqrt{\frac{5}{9}}r_{4,0} + \sqrt{\frac{2}{9}}r_{4,1}$

^aIt may be proved that $r_{l-1} = r_{l,1}$ from $\mu_{l=k}(k,0) = 0$.

$$I_{N,N^+}(\theta_k, \phi_k) = \sum_k S^k(N, N^+) \sum_{p,m} \sum_{l,l'} \begin{pmatrix} l & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} \\ \times \begin{pmatrix} l' & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} \mu_{l'}(k, q)^* \mu_l(k, q) \\ \times Y_{l'm}^*(\theta_k, \phi_k) Y_{lm}(\theta_k, \phi_k), \quad (22)$$

where k is even and l, l' are odd for the $(\pm) \leftrightarrow (\pm)$ transition, and k is odd and l, l' are even for the $(\pm) \leftrightarrow (\mp)$ transition. In Eq. (22), the generalized rotational line strength factor $S^k(N, N^+)$ has been disentangled from the multipole moments and from the angular part by applying

$$I_{N,N^+}(\theta_k, \phi_k) = (2N+1)(2N^++1) \sum_{k,k'} \sum_{l,m} \sum_{l',m'} \sum_{M_N, M_N^+} n(N, M_N) (-1)^{m-m'} [(2k+1)(2k'+1)]^{1/2} \\ \times \begin{pmatrix} l & 1 & k \\ -m & \mu_0 & -p \end{pmatrix} \begin{pmatrix} l' & 1 & k' \\ -m' & \mu_0 & -p' \end{pmatrix} \begin{pmatrix} N & k & N^+ \\ M_N & p & -M_N^+ \end{pmatrix} \begin{pmatrix} N & k' & N^+ \\ M_N & p' & -M_N^+ \end{pmatrix} \begin{pmatrix} N & k & N^+ \\ \Lambda & q & -\Lambda^+ \end{pmatrix} \\ \times \begin{pmatrix} N & k' & N^+ \\ \Lambda & q & -\Lambda^+ \end{pmatrix} \mu_{l'}(k', q)^* \mu_l(k, q) Y_{l'm'}^*(\theta_k, \phi_k) Y_{lm}(\theta_k, \phi_k). \quad (23)$$

Here we have coherent contributions from the reduced multipole moments with all possible l and k quantum numbers. In Eqs. (22) and (23), the angular part $Y_{lm}(\theta_k, \phi_k)$

TABLE III. The relations between the reduced multipole moments $\mu_l(k, q)$ and the dipole moments r_{Λ} for $\Delta\Lambda = \pm 1$ transitions.

Photoelectron partial wave	Relation
s wave ($l=0$)	$\mu_0(1, \pm 1) = r_{0,0}$
p wave ($l=1$)	$0 = r_{1,\pm 1} + r_{1,0}$ $\mu_1(2, \pm 1) = \sqrt{\frac{1}{2}} r_{1,\pm 1} + \sqrt{\frac{1}{2}} r_{1,0}$
d wave ($l=2$)	$\mu_2(1, \pm 1) = \sqrt{\frac{6}{10}} r_{2,\pm 2} - \sqrt{\frac{3}{10}} r_{2,\pm 1} + \sqrt{\frac{1}{10}} r_{2,0}$ $0 = \sqrt{\frac{2}{6}} r_{2,\pm 2} + \sqrt{\frac{1}{6}} r_{2,\pm 1} - \sqrt{\frac{3}{6}} r_{2,0}$ $\mu_2(3, \pm 1) = \sqrt{\frac{1}{15}} r_{2,\pm 2} + \sqrt{\frac{8}{15}} r_{2,\pm 1} + \sqrt{\frac{6}{15}} r_{2,0}$
f wave ($l=3$)	$\mu_3(2, \pm 1) = \sqrt{\frac{10}{21}} r_{3,\pm 2} - \sqrt{\frac{8}{21}} r_{3,\pm 1} + \sqrt{\frac{3}{21}} r_{3,0}$ $0 = \sqrt{\frac{5}{12}} r_{3,\pm 2} + \sqrt{\frac{1}{12}} r_{3,\pm 1} - \sqrt{\frac{6}{12}} r_{3,0}$ $\mu_3(4, \pm 1) = \sqrt{\frac{3}{28}} r_{3,\pm 2} + \sqrt{\frac{15}{28}} r_{3,\pm 1} + \sqrt{\frac{10}{28}} r_{3,0}$
g wave ($l=4$)	$\mu_4(3, \pm 1) = \sqrt{\frac{5}{12}} r_{4,\pm 2} - \sqrt{\frac{5}{12}} r_{4,\pm 1} + \sqrt{\frac{2}{12}} r_{4,0}$ $0 = \sqrt{\frac{9}{20}} r_{4,\pm 2} + \sqrt{\frac{1}{20}} r_{4,\pm 1} - \sqrt{\frac{10}{20}} r_{4,0}$ $\mu_4(5, \pm 1) = \sqrt{\frac{2}{15}} r_{4,\pm 2} + \sqrt{\frac{8}{15}} r_{4,\pm 1} + \sqrt{\frac{5}{15}} r_{4,0}$

the orthogonality relation of Eq. (2.32) of Ref. 12. Consequently, an incoherent sum of k values results. In Eq. (22), there is interference only between the reduced multipole moment terms with different values of l and l' for the same k value.

For angle-resolved photoionization from an anisotropic initial state, we do not have the orthogonality relation to eliminate cross terms between the reduced multipole moments with different ranks k and k' . Consequently, the angle-resolved photoelectron intensity distribution for an $N \rightarrow N^+$ transition has a complex form

$Y_{l'm'}^*(\theta_k, \phi_k)$ can be further simplified into a sum of $\beta_{LM} Y_{LM}(\theta_k, \phi_k)$ terms using the spherical harmonic addition theorem. The β_{LM} parameters obtained from analyzing photoelectron angular distributions can be related to reduced multipole moment elements and corresponding coefficients in a similar way as that described in Ref. 4(c).

TABLE IV. The relations between the reduced multipole moments $\mu_l(k, q)$ and the dipole moments r_{Λ} for $\Delta\Lambda = \pm 2$ transitions.

Photoelectron partial wave	Relation
s wave ($l=0$)	...
p wave ($l=1$)	$\mu_1(2, \pm 1) = r_{1,\pm 1}$
d wave ($l=2$)	$0 = \sqrt{\frac{2}{3}} r_{2,\pm 2} - \sqrt{\frac{1}{3}} r_{2,\pm 1}$ $\mu_2(3, \pm 2) = \sqrt{\frac{1}{3}} r_{2,\pm 2} + \sqrt{\frac{2}{3}} r_{2,\pm 1}$
f wave ($l=3$)	$\mu_3(2, \pm 2) = \sqrt{\frac{15}{21}} r_{3,\pm 2} - \sqrt{\frac{5}{21}} r_{3,\pm 1} + \sqrt{\frac{1}{21}} r_{3,0}$ $0 = \sqrt{\frac{3}{12}} r_{3,\pm 3} + \sqrt{\frac{4}{12}} r_{3,\pm 2} - \sqrt{\frac{5}{12}} r_{3,\pm 1}$ $\mu_3(4, \pm 2) = \sqrt{\frac{1}{28}} r_{3,\pm 3} + \sqrt{\frac{12}{28}} r_{3,\pm 2} + \sqrt{\frac{15}{28}} r_{3,0}$
g wave ($l=4$)	$\mu_4(3, \pm 2) = \sqrt{\frac{7}{12}} r_{4,\pm 3} - \sqrt{\frac{4}{12}} r_{4,\pm 2} + \sqrt{\frac{1}{12}} r_{4,\pm 1}$ $0 = \sqrt{\frac{7}{20}} r_{4,\pm 3} + \sqrt{\frac{4}{20}} r_{4,\pm 2} - \sqrt{\frac{9}{20}} r_{4,\pm 1}$ $\mu_4(5, \pm 2) = \sqrt{\frac{1}{15}} r_{4,\pm 3} + \sqrt{\frac{7}{15}} r_{4,\pm 2} + \sqrt{\frac{7}{15}} r_{4,\pm 1}$

Examination of Eqs. (16), (20), (22), and (23) shows the following. When the initial state is anisotropic, coherent contributions occur from different ranks k of reduced multipole moments. For the angle-resolved photoelectron intensity, the coherent contribution also occurs from different partial waves l . In previous treatments, the coherent terms between the dipole moments $r_{\lambda k}$ with different λ values, called λ interferences, do not appear in the above equations because they are absorbed into the $\mu_l(k, q)$ in the relations shown in Tables II, III, and IV.

III. APPLICATIONS

The angle-integrated photoionization probability for an $N \rightarrow N^+$ transition from an isotropic initial state appears simply to be an incoherent sum of the squares of multipole moment matrix elements multiplied by their corresponding generalized rotational line strength factors, as shown in Eq. (16). These multipole moment matrix elements are the only adjustable parameters necessary for fitting the rotational intensity distribution. In the following two examples, we demonstrate the use of Eq. (16). The first example is the rotationally resolved photoelectron spectra from the one-photon ionization of H_2 .^{34,35,6(b)} The second example is the rotationally resolved photoelectron spectra from the $(1+1')$ REMPI of NO.^{4(b)}

Rotationally resolved photoelectron spectra of H_2 were initially recorded by Åsbrink³⁴ using a Ne I light source and subsequently measured a decade later by Morioka *et al.*³⁵ with a He I light source. Recently, Merkt and Softley^{6(b)} have obtained the high-resolution ZEKE photoelectron spectrum of H_2 using a coherent XUV source. Itikawa^{26(b)} has carried out *ab initio* calculations on the photoionization of H_2 with attention to how the vibrational motion influences the spectrum. In his work, the dipole moment matrix elements for each partial wave are computed and then substituted into the traditional formula to obtain rotational line strengths. Merkt and Softley have compared these data with their own measurements for deduced rotational intensities of the transition $H_2 X^1\Sigma_g^+ v=0 \rightarrow H_2^+ X^2\Sigma_g^+ v^+=2$ and the results are listed in Table V.

As shown in Table V, only $\Delta N=0, \pm 2$ transitions are observed. Therefore, we need to consider the reduced multipole moments with $k \leq 2$. In addition, the k -even selection rule for a $g \leftrightarrow g$ transition further restricts k to have the two values 0 and 2. The H_2 sample is isotropic and is described by a Boltzmann distribution at 300 K. Therefore, the angle-integrated photoionization intensity for an $N \rightarrow N^+$ transition is given by

$$P(N, N^+) = (2 - (-1)^N) \exp\left(-\frac{B_0 N(N+1)}{kT}\right) \times (2N+1)(2N^++1) \frac{1}{3} \left[\frac{\delta_{NN^+}}{2N+1} |\bar{\mu}(0,0)|^2 + \left(\begin{matrix} N & 2 & N^+ \\ 0 & 0 & 0 \end{matrix} \right)^2 |\bar{\mu}(2,0)|^2 \right], \quad (24)$$

where the first factor $(2 - (-1)^N)$ takes into account the 3:1 nuclear spin degeneracy corresponding to the odd level vs the even level, the second factor is the Boltzmann term, and the remaining factors come from Eq. (16). Although the two factors $|\bar{\mu}(2,0)|^2$ and $|\bar{\mu}(0,0)|^2$ appear in Eq. (24), only one is independent in fitting the relative intensity distribution. Following the convention in Table V, we choose the most intense line as a constant, i.e., $P(1,1) = 100$. Then a fit is made to Eq. (24).

We first fit the *ab initio* rotational intensity distribution and find that $|\bar{\mu}(2,0)|^2/|\bar{\mu}(0,0)|^2 = 0.152$. Our calculated line intensities from the ratio of these two parameters agree with the results of Itikawa within the first three digits; see Table V. This agreement is not surprising because our simplified expression for the relative line intensities differs only formally from Itikawa's result. The *ab initio* calculation provides numerical values for several diode moments, but only one consolidated number is independent and decisive in determining the relative rotational intensity distribution. We also fit the ZEKE rotational intensity distribution to Eq. (24) excluding the (0-0), (2-0), and (0-2) transitions because these transitions have been reported by Merkt and Softley^{6(b)} to be perturbed. From this fit we find $|\bar{\mu}(2,0)|^2/|\bar{\mu}(0,0)|^2 = 0.173$. Our best fit to the ZEKE rotational intensity distribution agrees well with experiment, as shown in Fig. 1, when the perturbed lines are excluded.

For $(n+1)$ REMPI, the intermediate state is usually populated anisotropically. In the experiment of the $(1+1')$ REMPI of NO, Leahy, Reid, and Zare^{4(b)} have chosen the first laser beam polarized relative to the second laser by an angle of 54.7° . As a result of the choice of this "magic angle," the $N=22$ level of NO $A^2\Sigma^+ v=1$ is prepared with a constant equal population of its sublevels via the $P_{21}+Q_1(22.5)$ transition. A relative phase is also introduced among the sublevels, which causes the angular distribution of photoelectrons to be skewed. However, these interference effects vanish in the angle-integrated relative intensities for the $N \rightarrow N^+$ transitions which are approximately proportional to the β_{00} in the angular distribution. Consequently, we may treat the $N=22$ level as isotropic, and apply Eq. (16) to express the transition probabilities.

The $\Delta N=0, \pm 1, \pm 2$ transitions observed experimentally suggest that the reduced multipole moments with $k=0, 1$, and 2 should be considered. Parity selection rules further constrain the contributions from the multipole moments so that $|\bar{\mu}(2,0)|^2$ contributes to the $\Delta N=\pm 2$ transitions, $|\bar{\mu}(1,0)|^2$ to the $\Delta N=\pm 1$ transition, and both $|\bar{\mu}(0,0)|^2$ and $|\bar{\mu}(2,0)|^2$ to the $\Delta N=0$ transition. Specifically, we have

$$P(N, N-2) = \frac{N(N+1)}{2(2N-1)} |\bar{\mu}(2,0)|^2, \quad (25a)$$

$$P(N, N-1) = \frac{N}{3} |\bar{\mu}(1,0)|^2, \quad (25b)$$

TABLE V. Rotational line intensities from the one-photon ionization of H_2 at 300 K. Experimental results are from ZEKE, Ne I, and He I photoelectron spectra, and theoretical results are from *ab initio* calculations and from our best fit of the ZEKE and *ab initio* data to Eq. (24).

Transitions $N^+ - N$	Merkel and Softley [Ref. 6(b)]	Åsbrink (Ref. 33)	Morioka <i>et al.</i> (Ref. 34)	Itikawa [Ref. 26(b)]	Our fit	
	ZEKE	Ne I	He I	<i>ab initio</i>	ZEKE	<i>ab initio</i>
0-0	15*	42	27	18.5	18	18.5
2-0	51*	6.2	10.5	2.81	3.2	2.81
1-1	100	100	100	100	100	100
3-1	9.5	4.5	...	8.59	9.7	8.59
0-2	8.3*	2.2	...	0.51	0.6	0.51
2-2	20	31	21	17.5	18	17.5
1-3	0.50	0.6	0.50
3-3	16	15	14	13.3	14	13.3
5-3	1.1	0.93	1.1	0.93

*The 0-0, 2-0, and 0-2 transitions have been reported by Merkelt and Softley [Ref. 6(b)] to be perturbed.

$$P(N, N) = \frac{2N+1}{3} |\bar{\mu}(0,0)|^2 + \frac{N(N+1)(2N+1)}{3(2N+3)(2N-1)} |\bar{\mu}(2,0)|^2, \quad (25c)$$

$$P(N, N+1) = \frac{N+1}{3} |\bar{\mu}(1,0)|^2, \quad (25d)$$

and

$$P(N, N+2) = \frac{(N+1)(N+2)}{2(2N+3)} |\bar{\mu}(2,0)|^2. \quad (25e)$$

In Eq. (25), there are two independent parameters among the three reduced multipole moments. Using the previous convention that $P(22,22)=100$, we find that $|\bar{\mu}(1,0)|^2/|\bar{\mu}(0,0)|^2=0.103$ and $|\bar{\mu}(2,0)|^2/|\bar{\mu}(0,0)|^2=0.340$. Figure 2 compares the experimental relative distribution of the

angle-integrated photoelectron intensities with that obtained from this fit. Once again the close agreement is quite pleasing.

IV. CONCLUDING REMARKS

We have derived in this paper simple expressions for the rotationally resolved photoelectron intensity distribution when a sample of isotropic diatomic molecules is photoionized by a beam of pure polarized light. This treatment relies on regrouping the interaction of the dipole photon and the ejected electron so that the probability of an $N \rightarrow N^+$ transition becomes proportional to the sum of the product of a generalized rotational line strength factor times the reduced multipole moment. The generalized rotational line strength are readily computed, whereas values of the independent reduced multipole moments can be de-

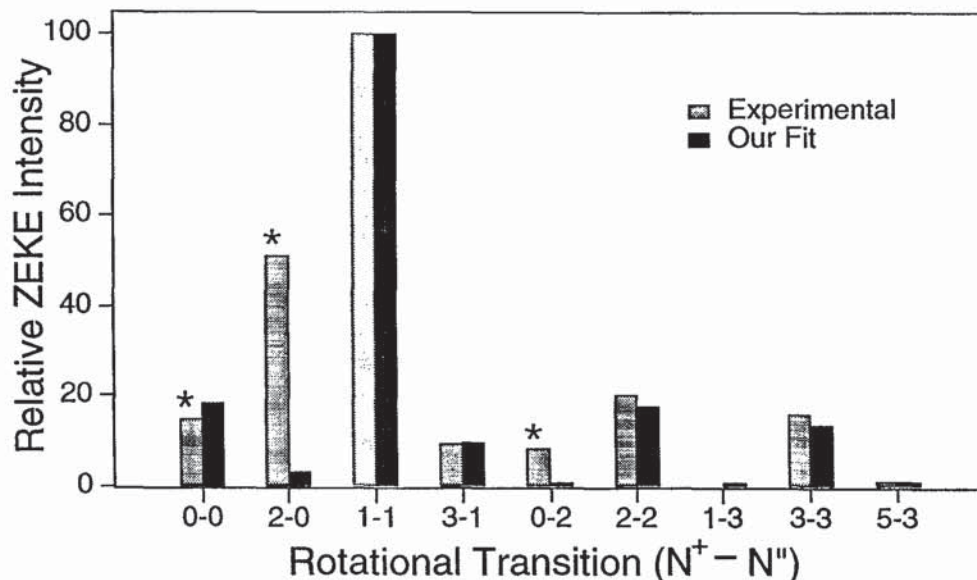


FIG. 1. Relative line intensities of the one-photon $H_2 X^1\Sigma_g^+ v''=0, N'' \rightarrow H_2^+ X^2\Sigma_g^+ v^+=2, N^+$ ZEKE spectrum. The experimental data are taken from the work of Merkelt and Softley [Ref. 6(b)]. They are fit to Eq. (24) for a sample temperature of 300 K excluding perturbed lines marked by asterisks in the figure.

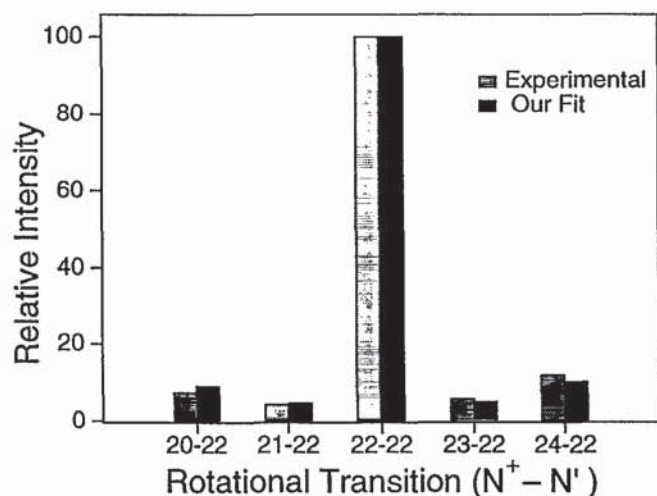


FIG. 2. Relative intensities of the photoelectron spectrum for the process $\text{NO } A^2\Sigma^+ v'=1, N'=22 \rightarrow \text{NO}^+ X^1\Sigma^+ v^+=1, N^+$. The ions are produced by $(1+1')$ REMPI via the $P_{21}+Q_1(22.5)$ transition for an angle of 54.7° between the polarization vectors of the two laser beams. The experimental data are taken from Leahy *et al.* [Ref. 4(b)] by integrating the reported angular distributions. They are fit to Eq. (25).

duced from a best least square fit to the experimentally determined photoelectron intensity distribution.

This treatment is applicable to many other transition processes provided that the Born–Oppenheimer separation of nuclear rotational motion from other motions is valid. For example, the procedure can also be applied to describe electron impact ionization and the same generalized rotational line strength factors result. Many other generalizations are also possible, such as the inclusion of different angular momentum coupling cases and the extension to polyatomic systems.

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¹D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy, A Handbook of He 584 Å Spectra* (Interscience, New York, 1970); J. H. D. Eland, *Photoelectron Spectroscopy* (Wiley-Halsted, New York, 1974); J. Berkowitz, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy* (Academic, New York, 1979).

²S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, *J. Chem. Phys.* **78**, 4315 (1983); **86**, 1727 (1987); M. A. O'Halloran, S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, *ibid.* **87**, 3288 (1987).

- ³W. G. Wilson, K. S. Viswanathan, E. Sekreta, and J. P. Reilly, *J. Phys. Chem.* **88**, 672 (1984); K. S. Viswanathan, E. Sekreta, E. R. Davidson, and J. P. Reilly, *J. Chem. Phys.* **90**, 5078 (1986); X. Song, E. Sekreta, J. P. Reilly, H. Rudolph, and V. McKoy, *ibid.* **91**, 6062 (1989).
- ⁴(a)S. W. Allendorf, D. J. Leahy, D. C. Jacobs, and R. N. Zare, *J. Chem. Phys.* **91**, 2216 (1989); (b)D. J. Leahy, K. L. Reid, and R. N. Zare, *ibid.* **95**, 1757 (1991); (c)K. L. Reid, D. J. Leahy, and R. N. Zare, *ibid.* **95**, 1746 (1991); (d)K. L. Reid, D. J. Leahy, and R. N. Zare, *Phys. Rev. Lett.* (in press).
- ⁵K. Müller-Dethlefs, M. Sander, and E. W. Schlag, *Chem. Phys. Lett.* **112**, 291 (1984); M. Sander, L. A. Chewter, K. Müller-Dethlefs, and E. W. Schlag, *Phys. Rev. A* **36**, 4543 (1987); L. A. Chewter, M. Sander, K. Müller-Dethlefs, and E. W. Schlag, *J. Chem. Phys.* **86**, 4737 (1987); W. Habenicht, G. Reiser, and K. Müller-Dethlefs, *ibid.* **95**, 4809 (1991).
- ⁶(a)H. H. Fielding, T. P. Softley, and F. Merkt, *Chem. Phys.* **155**, 257 (1991); (b)F. Merkt and T. P. Softley, *J. Chem. Phys.* **96**, 4149 (1992).
- ⁷R. G. Tonkyn, J. W. Winniczek, and M. G. White, *Chem. Phys. Lett.* **164**, 137 (1989).
- ⁸A. Fujii, T. Ebata, and M. Ito, *J. Chem. Phys.* **88**, 5307 (1988); *Chem. Phys. Lett.* **161**, 93 (1989).
- ⁹J. Xie and R. N. Zare, *Chem. Phys. Lett.* **159**, 399 (1989); (in preparation).
- ¹⁰H. Hönl and F. London, *Z. Phys.* **33**, 803 (1925).
- ¹¹I. Kovács, *Rotational Structure in the Spectra of Diatomic Molecules* (American Elsevier, New York, 1969).
- ¹²R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
- ¹³G. Placzek and E. Teller, *Z. Phys.* **81**, 209 (1933).
- ¹⁴R. G. Bray and R. M. Hochstrasser, *Mol. Phys.* **31**, 1199 (1976).
- ¹⁵W. M. McClain and R. A. Harris, *Excited States*, edited by E. C. Lim (Academic, New York, 1977), Vol. 3, pp. 1–56.
- ¹⁶K. Chen and E. S. Yeung, *J. Chem. Phys.* **69**, 43 (1977).
- ¹⁷F. Metz, W. E. Howard, L. Wunsch, H. J. Neusser, and E. W. Schlag, *Proc. R. Soc. London, Ser. A* **363**, 381 (1978).
- ¹⁸A. C. Kummel, G. O. Sitz, and R. N. Zare, *J. Chem. Phys.* **85**, 6874 (1986); **88**, 6707 (1988); **88**, 7357 (1988); J. R. Waldeck, A. C. Kummel, G. O. Sitz, and R. N. Zare, *ibid.* **90**, 4112 (1989).
- ¹⁹J. B. Halpern, H. Zacharias, and R. Wallenstein, *J. Mol. Spectrosc.* **79**, 1 (1980).
- ²⁰G. C. Nieman, *J. Chem. Phys.* **75**, 584 (1981).
- ²¹R. N. Dixon, J. M. Bayley, and M. N. R. Ashfold, *Chem. Phys.* **84**, 21 (1984).
- ²²C. Mainos, *Phys. Rev. A* **33**, 3983 (1986).
- ²³Y.-N. Chiu, *J. Chem. Phys.* **86**, 1686 (1987).
- ²⁴U. Fano, *Phys. Rev. A* **2**, 353 (1970); U. Fano and D. Dill, *ibid.* **6**, 185 (1972); J. L. Dehmer and D. Dill, *J. Chem. Phys.* **65**, 5327 (1976).
- ²⁵A. D. Buckingham, B. J. Orr, and J. M. Sichel, *Phil. Trans. R. Soc. London, Ser. A* **268**, 147 (1970).
- ²⁶(a)Y. Itikawa, *Chem. Phys.* **28**, 461 (1978); (b)**30**, 109 (1978).
- ²⁷J. C. Hansen and R. S. Berry, *J. Chem. Phys.* **80**, 4078 (1984).
- ²⁸S. N. Dixit and V. McKoy, *J. Chem. Phys.* **82**, 3546 (1985); *Chem. Phys. Lett.* **128**, 49 (1986); K. Wang and V. McKoy, *J. Chem. Phys.* **95**, 4977 (1991).
- ²⁹N. A. Cherepkov, *Adv. At. Mol. Phys.* **19**, 395 (1983); G. Raseev and N. A. Cherepkov, *Phys. Rev. A* **42**, 3948 (1990).
- ³⁰K. Müller-Dethlefs, *J. Chem. Phys.* **95**, 4821 (1991).
- ³¹R. D. Gilbert and M. S. Child, *Chem. Phys. Lett.* **287**, 153 (1991).
- ³²J. Xie and R. N. Zare, *J. Chem. Phys.* **93**, 3033 (1990).
- ³³The correspondence between Buckingham, Orr, and Sichel (Ref. 25) and the present work is as follows: $K \rightarrow N$; $j \rightarrow k$; $\lambda \rightarrow l$; $m_\lambda \rightarrow \lambda$; $m' \rightarrow \mu$; and $\Delta\lambda \rightarrow q$. We are grateful to T. P. Softley for calling our attention to this equivalence.
- ³⁴L. Åsbrink, *Chem. Phys. Lett.* **7**, 549 (1970).
- ³⁵Y. Morioka, S. Hara, and M. Nakamura, *Phys. Rev. A* **22**, 177 (1980).