Rotationally resolved photoionization of polyatomic hydrides: CH₃, H₂O, H₂S, H₂CO

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Rotationally resolved photoionization of polyatomic hydrides: CH₃, H₂O, H₂S, H₂CO

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Combined theoretical and experimental studies of rotationally resolved photoelectron spectra for single-photon ionization of the outermost valence orbitals of H₂O, H₂S, H₂CO, and CH₃ are reported. Agreement between calculated and measured spectra is very encouraging. Both show that photoionization dynamics is very molecular in origin for H₂O, H₂S, and H₂CO but quite atomicleike for CH₃. Parity selection rules and the angular momentum composition of the photoelectron are used to illustrate the dynamical aspects of photoionization of polyatomics as molecular symmetry changes in a group of structurally related systems.

I. INTRODUCTION

Recent studies of rotationally resolved photoionization of the nonlinear molecules H₂O (Refs. 1–3), H₂S (Refs. 4–6), and CH₃ (methyl radical)⁷ highlight the unique aspects of molecular photoionization as a probe of electron–core interactions at short range. Specifically, *K*-state resolution of the rotational structure in polyatomic cations allows resolution of the degenerate photoelectron final angular momentum states by parity, i.e., *l*=even or *l*=odd. As in all photofragmentation processes, determination of the final state distributions of the fragments (photoelectron and cation in this case) provides a dynamical window on the electronic and nuclear motions of the “collision complex” responsible for the asymptotic fragment distributions. In photoionization, the collision complex corresponds to the photoelectron and ion core at short range where the anisotropy of the molecular cation potential determines the partial wave distribution that the electron will be “scattered” into at long range. The short- to long-range evolution of the photoelectron leads to spectroscopic properties which are appropriate for *l*-uncoupled Rydberg (high-*n*) or continuum transitions, but which ultimately reflect the symmetry of the cation potential.

In this work, we present new experimental and theoretical results for single-photon ionization of the related polyatomic molecule, H₂CO (formaldehyde), as well as theoretical calculations for the methyl radical whose experimental spectrum has been recently published.⁷ Although H₂O, H₂S, and H₂CO are all planar (*C*_{2v}) in their neutral and ionic ground states, the symmetry of the outermost 2*b*₂ orbital of formaldehyde and the assignment of its principal axes leads to significant differences in the types of rotational transitions that are observed. Earlier experimental and theoretical work for H₂O and H₂S are also included to illustrate the dynamical aspects of photoionization of polyatomics as molecular symmetry changes in a group of structurally related systems.

II. THEORY: FORMULATION AND CALCULATIONS

As noted above, photofragmentation dynamics refers primarily to the nature and fate of the collision complex which is produced by photoexcitation. Because photoabsorption takes place at short range, the photoionization collision complex consists of the molecular ion core and a strongly coupled photoexcited electron. The dynamics of this short-range collision complex is governed by the usual bound-bound selection rules governing dipole transitions, e.g., $\Delta J = 0, \pm 1$, as well as other propensity rules which depend on specific angular momentum coupling cases. As fragmentation proceeds and the photoelectron moves into the asymptotic region, the electron–core interaction becomes less anisotropic and the angular momentum coupling becomes more appropriate to a photoelectron of well defined orbital angular momentum and a specific rovibronic level of the ion core. This uncoupling can be viewed as a scattering process in which the photoexcited electron exchanges energy and angular momentum with the ion core. The net result is that changes in core angular momentum well beyond $\Delta J = 0, \pm 1$ are possible. For absorption of a single photon, conservation of angular momentum requires only that

$$\Delta J = J_+ - J_i = l + 3/2, l + 1/2, \dots, -l - 3/2, \quad (1)$$

where *l* is the orbital angular momentum associated with *ks, kp, kd, ...* partial waves and where the photoelectron spin (*s* = ±1/2) and photon angular momentum (1) result in the ±3/2 term. This simple expression highlights the relationship between the observable rotational branch transitions of the core, given by ΔJ , and the unobserved partial wave composition (*l*) of the outgoing photoelectron. This is a key result and is a significant motivation for pursuing rotationally resolved measurements. In what follows, we develop the theoretical basis for interpreting rotationally resolved photoionization with particular emphasis on those aspects which are unique to nonlinear molecules.

^{a)}Contribution No. 8888.

A. Differential cross section

Under collision-free conditions, the rotationally resolved differential cross section for single-photon ionization of a rotational level of the ground state of a molecule by linearly polarized light can be written as

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)], \quad (2)$$

where σ is the total cross section, β the asymmetry parameter, and $P_2(\cos \theta)$ the Legendre polynomial. Here the total cross section σ and asymmetry parameter β have the form^{2,3}

$$\sigma \propto \sum_{lm} \rho_{M_J M_{J_+}} |C_{lm}(M_J M_{J_+})|^2, \quad (3)$$

and

$$\begin{aligned} \beta = \frac{5}{\sigma} \sum_{ll'm} (-1)^m (2l+1)(2l'+1) \rho_{M_J M_{J_+}} \\ \times C_{lm}(M_J M_{J_+}) C_{l'm}^*(M_J M_{J_+}) \\ \times \begin{pmatrix} l & l' & 2 \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix} \end{aligned} \quad (4)$$

where $\rho_{M_J M_{J_+}}$ is the population of the M_J sublevel of the ground state and $C_{lm}(M_J M_{J_+})$ is the coefficient for photoionization of the M_J level of the ground state leading to the

M_{J_+} level of the ion. An expression for $C_{lm}(M_J M_{J_+})$ has been derived by Lee *et al.*³ for molecules with C_{2v} symmetry and has the simple form

$$\begin{aligned} C_{lm}(M_J M_{J_+}) = \sum C [1 + (-1)^{\Delta N + \Delta p + l + 1}] \\ \times I_{hl\lambda\mu}^{\gamma q} \begin{pmatrix} N_t & 1 & l \\ -K_t & \mu & \lambda \end{pmatrix} \\ \times \left[\begin{pmatrix} N_+ & N_i & N_t \\ -K_+ & K_i & K_t \end{pmatrix} + (-1)^{p_+} \right. \\ \left. \times \begin{pmatrix} N_+ & N_i & N_t \\ K_+ & K_i & K_t \end{pmatrix} \right], \end{aligned} \quad (5)$$

with $\Delta N = N_+ - N_i$ and $\Delta p = p_+ - p_i$. In Eq. (5), C is a laboratory frame quantity given in Ref. 3, N is the total angular momentum (exclusive of spin), K is its projection on the z axis, p is the parity of the rotational wave function, N_t is the angular momentum transfer, l is an angular momentum component of the photoelectron, λ is its projection along the molecular z axis, μ is the light polarization index in the molecular frame, γ is one of the irreducible representations (IR) of the molecular point group, q is a component of this representation, and h distinguishes between different bases for the same IR corresponding to the same value of l .

A similar expression for $C_{lm}(M_J M_{J_+})$ of Eq. (5) has been derived by Wang and McKoy⁸ for the D_{3h} molecular symmetry group appropriate to CH_3 . It has the simple form

$$\begin{aligned} C_{lm}(M_J M_{J_+}) = \sum C' I_{hl\lambda\mu}^{\gamma q} \begin{pmatrix} N_t & 1 & l \\ -K_t & \mu & \lambda \end{pmatrix} \left[\begin{pmatrix} N_+ & N_i & N_t \\ -K_+ & K_i & K_t \end{pmatrix} + (-1)^{p_i} \begin{pmatrix} N_+ & N_i & N_t \\ -K_+ & -K_i & K_t \end{pmatrix} \right. \\ \left. + (-1)^{p_+} \begin{pmatrix} N_+ & N_i & N_t \\ K_+ & K_i & K_t \end{pmatrix} + (-1)^{p_i + p_+} \begin{pmatrix} N_+ & N_i & N_t \\ K_+ & -K_i & K_t \end{pmatrix} \right]. \end{aligned} \quad (6)$$

A central quantity in these studies is the matrix element $I_{hl\lambda\mu}^{\gamma q}$ for photoejection of an electron from a bound molecular orbital $\phi_i^{y'q'}$ into a photoelectron continuum orbital $\Psi_{f,k}^{(-)}(\mathbf{r})$. The partial wave components $\psi_{khl m}^{(-)\gamma q}$ of $\Psi_{f,k}^{(-)}(\mathbf{r})$ are defined by an expansion in generalized harmonics about $\hat{\mathbf{k}}$ of the photoelectron

$$\Psi_{f,k}^{(-)}(\mathbf{r}) = \left(\frac{2}{\pi} \right)^{1/2} \sum_{lm} i^l \psi_{khl m}^{(-)\gamma q}(\mathbf{r}) X_{hl m}^{*\gamma q}(\hat{\mathbf{k}}), \quad (7)$$

where $X_{hl m}^{*\gamma q}(\hat{\mathbf{k}})$ is a generalized harmonic. Single-center expansions of $\psi_{khl m}^{(-)\gamma q}(\mathbf{r})$ and $\phi_i^{y'q'}(\mathbf{r}')$, e.g.,

$$\psi_{khl m}^{(-)\gamma q} = \sum_{l'\lambda} g_{hl m, l'\lambda}^{\gamma q}(k, r) \mathcal{D}_{m\lambda}^{l'} X_{hl' \lambda}^{\gamma q}(\hat{\mathbf{r}}'), \quad (8)$$

define partial wave photoelectron matrix elements $I_{hl\lambda\mu}^{\gamma q}$ in the molecular frame for ionization out of orbital $\phi_i^{y'q'}(\mathbf{r}')$, i.e.,

$$\begin{aligned} I_{hl\lambda\mu}^{\gamma q} = \sum_{l', l_0} \langle g_{hl m, l'\lambda}^{\gamma q}(k, r) X_{hl' \lambda}^{\gamma q}(\hat{\mathbf{r}}') | r Y_{1\mu}(\hat{\mathbf{r}}') \\ \times \phi_{ih' l_0}^{y'q'}(r) X_{h' l_0 \lambda_0}^{y'q'}(\hat{\mathbf{r}}') \rangle, \end{aligned} \quad (9)$$

where $\mathcal{D}_{m\lambda}^{l'}$ is a rotational matrix in Edmonds' notation.⁹ Whereas only $l=l'$ terms are allowed in Eq. (9) for the central fields of atomic systems, where the angular momentum of the photoelectron must be conserved, $l \neq l'$ terms arise in Eq. (9) due to the nonspherical molecular ion potentials. Note that, in addition to these $l \neq l'$ terms, terms with $m \neq \lambda$ also arise in Eq. (9) reflecting the lower symmetry of nonlinear molecules. The use of molecular photoelectron orbitals which correctly incorporate such angular momentum coupling is essential at the low photoelectron energies of interest here.

B. Parity selection rules

The general form for the parity selection rule connecting specific rovibronic states of the neutral and ion for linear molecules is given by^{10–12}

$$\Delta J + \Delta S + \Delta p + l = \text{even}, \quad (10)$$

where $\Delta S = S_+ - S_i$ and where $\Delta p = p_+ - p_i$ represents the change in Kronig parity of the initial and final electronic states ($p = 0$ for Λ^+ or 1 for Λ^-). The utility of this expression is that it directly relates different photoelectron partial waves ($l = \text{even or odd}$) to different branch transitions corresponding to a specific ΔJ and parity change. Specifically, if one spectrally resolves the parity components of the upper and lower rotational levels, it is possible to separate the $l = \text{even}$ and $l = \text{odd}$ contributions to the photoelectron matrix element. Examples of molecules where rotational levels of different parity can be resolved include H_2 and CO , both of which involve $^2\Sigma^+ \leftarrow ^1\Sigma^+$ photoionization transitions.^{13–15} For upper and lower Hund's case (b) Σ^+ states, Eq. (10) reduces to $\Delta N + l = \text{odd}$.¹⁰ This selection rule dictates that the Q branch ($\Delta N = 0$) be associated with odd partial waves while the P and R branches ($\Delta N = \pm 1$) reflect contributions of even partial waves in the continuum.

In generalizing the angular momentum and parity constraints for photoionization in nonlinear polyatomic molecules, it is necessary to consider the additional quantum numbers required to specify individual rovibronic quantum states. In general, polyatomic molecules have three independent axes of rotation labeled in order of increasing moment of inertia ($I_a < I_b < I_c$). Consequently, there are three body-fixed projections of the total angular momentum (K_a, K_b, K_c), two of which are required in specifying a single rotational level, e.g., $|JK_a K_c\rangle$. In addition to conservation of the total angular momentum given by Eq. (1), the projections of J (or N) on the molecule-fixed quantization axis are also conserved. The general form of this selection rule (not including spin) is given by^{2,3}

$$\Delta K_\eta = \mu + \lambda, \quad (11)$$

where η represents the rotation axis of highest symmetry (body-fixed z axis) and λ and μ are the η -axis projections of the photoelectron orbital angular momentum and the photon angular momentum ($\mu = 1, 0, -1$). For diatomic molecules, in which the rotational angular momentum (R) lies perpendicular to the internuclear axis, Eq. (11) takes the simple form $\Delta \Lambda = \lambda, \lambda \pm 1$.

In bound-state spectroscopy of diatomics involving valence or low- n Rydberg states, transitions are characterized as parallel or perpendicular depending on whether the transition dipole lies along ($\Delta \Lambda = 0$) or is perpendicular to ($\Delta \Lambda = \pm 1$) the internuclear axis. Due to the asymptotic uncoupling of the core and photoelectron angular momenta, photoionization transitions allow for a larger range of $\Delta \Lambda$ which are more conveniently classified as $\Delta \Lambda = \text{even}$ and $\Delta \Lambda = \text{odd}$. For symmetric tops, the subscript in Eq. (11) is suppressed and K represents the projection onto the a axis for prolate tops ($I_a < I_b = I_c$) and the c axis for oblate tops ($I_a = I_b < I_c$). In this case, $\Delta K = \text{even}$ and $\Delta K = \text{odd}$ photoionization transitions have much the same meaning as $\Delta \Lambda$ in

diatomic molecules. Unlike diatomic molecules, the rotational energy level spacings for symmetric tops includes energy terms proportional to both $J(J+1)$ and K^2 , such that the rotational state distribution of the cation clearly reflects the even or odd character of $|\Delta K|$. For asymmetric tops such as H_2O and H_2CO , three types of rotational transitions are classified by the four combinations of even/odd for $\Delta K_a/\Delta K_c$. Both ΔK_a and ΔK_c are odd or even in type b transitions, while type a transitions are characterized by $\Delta K_a = \text{even}$ and $\Delta K_c = \text{odd}$ and type c transitions by $\Delta K_a = \text{odd}$ and $\Delta K_c = \text{even}$. In bound-bound electronic transitions, these different types refer to the axes along which the transition dipole has a nonzero projection, i.e., $\mu_{f \leftarrow i} \parallel a$ -axis in type a transitions. The transition dipole is not uniquely determined in a photoionization transition as result of l uncoupling of the photoelectron from the body-fixed frame at long range. From the standpoint of parity, however, each unique specification of the transition type, i.e., $\Delta K = \text{even or odd}$, type a , type b , etc., is associated with a specific parity of the photoelectron, $l = \text{odd or } l = \text{even}$. As will be seen below, complete K state resolution provides unique information concerning the photoionization dynamics of polyatomic molecules.

C. Computational details

The ground state wave functions of H_2O , H_2S , H_2CO , and CH_3 were obtained at the self-consistent-field (SCF) level at their equilibrium geometries.¹⁶ The basis set consists of a $[5s4p]$ contraction of the $(10s6p)$ primitive Cartesian Gaussian functions of Dunning¹⁷ augmented by two s ($\alpha = 0.028$ and 0.003), two p ($\alpha = 0.021$ and 0.002), and three d ($\alpha = 1.322, 0.3916$, and 0.09) functions on the oxygen atom. On the sulfur atom, a $[6s4p]$ contraction of the $(12s9p)$ primitive Cartesian Gaussian functions of McLean and Chandler,¹⁸ augmented with two s ($\alpha = 0.035$ and 0.0088), two p ($\alpha = 0.025$ and 0.0035), and four d ($\alpha = 1.28, 0.36, 0.088$, and 0.015) functions, was used. The basis for the carbon atom consists of a $[9s5p/5s3p]$ basis of Dunning¹⁹ augmented with one s ($\alpha = 0.075$), one p ($\alpha = 0.05$), and three d ($\alpha = 0.95, 0.25$, and 0.08) functions. On the hydrogen atom, we used a $[3s1p]$ contraction of the $(4s2p)$ primitive Gaussian functions of Dunning^{17,19,20} augmented with one s ($\alpha = 0.05$) and two p ($\alpha = 1.12$ and 0.1296) functions for H_2S , H_2CO , and CH_3 (see Refs. 2 and 3 for H_2O). For H_2CO , the basis set is further augmented with two s ($\alpha = 0.095$ and 0.025) functions, two p ($\alpha = 0.095$ and 0.025) functions, and one d ($\alpha = 0.095$) function at the center of mass. With these basis sets, the total SCF energies were $-76.052\,376$ a.u. for H_2O , $-398.706\,389$ a.u. for H_2S , $-113.909\,500$ a.u. for H_2CO , and $-39.570\,507$ a.u. for CH_3 . Single-center expansion of the outermost valence orbital of these molecules reveals that the $1b_1$ orbital of H_2O has 99.7% p and 0.3% d character, the $2b_1$ orbital of H_2S has 99.8% p and 0.2% d character, the $2b_2$ orbital of H_2CO has 4.8% p , 80.0% d , 3.7% f , 9.1% g ($l_0 = 4$), and 1.5% h ($l_0 = 5$) character, and the $1a_2''$ orbital of CH_3 has 99.9% p and 0.1% g ($l_0 = 4$) character.

The procedures for obtaining the photoelectron con-

tinuum orbitals used in these studies have been discussed previously.^{2,3} Briefly, we assume a frozen-core Hartree–Fock model in which the core orbitals are taken to be those of the ion and the photoelectron orbital is obtained as a solution of a one-electron Schrödinger equation. To obtain the photoelectron orbital, we have used an iterative procedure, based on the Schwinger variational principle,²¹ to solve the Lippmann–Schwinger equation. This procedure begins by approximating the static-exchange potential of the ionic core by a separable potential.²¹ The Lippmann–Schwinger equation with this separable potential can be readily solved and provides an approximate photoelectron orbital $\phi_k^{(0)}$. These $\phi_k^{(0)}$ can be iteratively improved to yield converged solutions to the Lippmann–Schwinger equation containing the exact static-exchange potential. In this work eight iterations were used to achieve converged solutions for the molecular photoelectron orbitals. Other details of the calculations for these molecules are similar to those for H₂O.^{2,3}

III. EXPERIMENT

The photoelectron spectrometer and coherent vacuum ultraviolet (vuv) source have been described in detail elsewhere.²² Briefly, we use a differentially pumped frequency-tripling chamber attached to a conventional photoelectron/photoion time-of-flight (TOF) spectrometer. Tunable vuv radiation suitable for one-photon ionization into the vibrationless ground ionic states was produced by nonresonant third harmonic generation in argon (98.3–98.1 nm, H₂O), nonresonant sum frequency generation ($2\omega_{uv} + \omega_{vis}$) in xenon (118.6–188.3 nm, H₂S) and resonant four-wave difference frequency mixing ($2\omega_{uv} - \omega_{vis}$) in krypton (126.5–125.7 nm, CH₃). Additional experimental details pertaining to the measurement of rotationally resolved threshold photoelectron spectra for H₂O, H₂S, and CH₃ can be found in previous publications.^{1,3,7} Nonresonant sum frequency generation associated with the $5s' \leftarrow 4p$ three-photon resonance in krypton was used to generate vuv radiation near 113.9 nm for photoionization to the $\tilde{X}^2B_2(000)$ ground state of H₂CO⁺. The vuv conversion efficiency for krypton in this wavelength region is at least 1 order of magnitude poorer than for the nearby $7s \leftarrow 5p$ transition in xenon which was used in our previous study of H₂S. Consequently, the signal level for the $(000)^+ \leftarrow (000)''$ vertical transition was comparatively small and measurements of vibrationally excited levels $[(001)^+ \text{ and } (010)^+]$ with considerably smaller Franck–Condon intensity²³ were not possible. The output of a Nd:YAG (Continuum YG-881, 20 Hz) pumped dye-laser (Quanta-Ray PDL-3) using Rhodamine 590 dye was frequency doubled (KDP crystal, INRAD Autotracker II) to produce the tunable uv (285.0–284.6 nm; ~5 mJ/pulse) and visible (570.0–569.2 nm; ~40 mJ/pulse) radiation for sum frequency mixing. The collinear visible and uv laser beams were focused by a 100 mm focal length achromatic lens (Optics for Research) inside the tripling chamber and into a pulsed, free jet expansion of krypton. The diverging fundamentals (visible and uv) and sum frequency vuv radiation are captured by a Pyrex capillary tube (30 cm long; 1 mm i.d.) and directed into the TOF spectrometer, where it passes between two parallel plates

which define the extraction field for the TOF spectrometer. The energy bandwidth of the vuv radiation was measured to be ~0.7 cm⁻¹ (FWHM).

Rotationally resolved threshold photoelectron spectra were obtained by delayed, pulsed-field ionization (PFI) which is a variant of zero-kinetic-energy (ZEKE) threshold photoelectron spectroscopy.²⁴ PFI takes advantage of the well known Stark shift of an ionization threshold in an external electric field. Bound Rydberg levels very near the ionization threshold, which are stable in a field-free environment, become open ionization channels when a Stark shift larger than their binding energy is applied. Continuity of oscillator strength across the ionization threshold ensures that the photoabsorption intensities into these Rydberg states just below threshold are a measure of the cross sections for photoionization just above threshold. In this work, field ionization is induced by a fast rising (~5 ns) voltage pulse applied 400 ns after the vuv photoexcitation laser pulse. Under these conditions field ionization takes place diabatically with a Stark shift of $\sim 4\sqrt{F}$ cm⁻¹ (F is the field strength in V/cm).²⁵ For the small pulsed field used here (0.55 V/cm), this Stark shift will cause field ionization of Rydberg levels with $n \geq 200$. Rydberg states with such high principal quantum numbers are very long lived as a consequence of rapid l and m_l mixing induced by a small dc electric field (~0.05 V).²⁵ The small dc voltage applied to the repeller plate also sweeps out any slow or near-ZEKE photoelectrons produced directly by the laser pulse. Electrons produced by field ionization are readily distinguished from prompt photoelectrons by their dependence on pulse voltage and delay. Wavelength spectra are obtained by gated integration of the electron TOF peak associated with field ionization as recorded by a CAMAC controlled 200 MHz transient digitizer (LeCroy 8828D).

The formaldehyde sample was produced by pyrolysis of paraformaldehyde at 380 K and trapping the formaldehyde vapor as a liquid in a glass U tube cooled to 200 K (dry ice/acetone slush). A ~3% mixture of H₂CO in Ar was produced by pressuring the cooled storage tube to 880 Torr. Supersonic expansion of this mixture through a pulsed valve (Laser Technics) fitted with a 0.5 mm diameter nozzle resulted in a molecular beam containing formaldehyde molecules with a rotational temperature of ~7 K (see Sec. IV A 2). A 1 mm skimmer located 1 cm downstream of the valve collimated the beam so it passed cleanly between the field ionization electrodes. In assigning rotationally cold spectra, we assume that the populations in the nuclear spin states (ortho and para) do not redistribute during the expansion. For normal H₂CO this fixes the ratio of ortho to para at 3:1, regardless of the final rotational temperature. The ortho and para nuclear spin manifolds are then treated separately, each with the same rotational temperature (relative to its lowest energy level) and then normalized to recover the overall 3(ortho):1(para) ratio.

The vuv radiation was energy calibrated to known rotational lines of the (3–0) band of the $C^1\Pi_u \leftarrow X^1\Sigma_g^+$ transition in H₂ detected via two-photon (vuv+uv) resonant enhanced multiphoton ionization (REMPI).²⁶ Wavelength spectra were then placed on an absolute energy scale by cor-

FIG. 1. Level structure of the first few rotational levels of H_2O and H_2O^+ . Overall rovibronic symmetries (Γ_{evr}) and parities (p_{evr}) are labeled for each level. Each level of the ion can be coupled to $l=\text{even}$ (e) and $l=\text{odd}$ (o) photoelectron partial waves to give an overall final state parity ($p_{\text{evr}l}$). A few examples of type a , b , and c transitions are also shown. Type b transitions are forbidden by nuclear spin statistics (Ref. 1).

recting for the small Stark shift ($1\text{--}2\text{ cm}^{-1}$) introduced by the pulsed field. Uncertainties in the wavelength calibration and spectral peak location result in an overall uncertainty of $\pm 2\text{ cm}^{-1}$ in the line positions.

IV. RESULTS AND DISCUSSION

A. Asymmetric tops: H_2X ($\text{X}=\text{O}, \text{S}, \text{CO}$)

The polyatomic molecules H_2O , H_2S , and H_2CO are planar asymmetric tops with C_{2v} symmetry. The outermost $1b_1$ ($2b_1$) orbital of H_2O (H_2S) is essentially a p -type atomic orbital, pointing out of the plane and centered on the oxygen (sulfur) atom. The outermost $2b_2$ orbital of formaldehyde lies in the molecular plane and is localized on the C–O moiety. The latter can be characterized as a d -type atomic orbital fixed at the center of mass. Given the atomlike nature of these orbitals, one might expect atomic selection rules ($\Delta l = \pm 1$) to provide a reasonable description of photoionization of these molecules. In the case of H_2O , earlier *ab initio* calculations indicate dominant ks ($l=0$) and kd ($l=2$) photoionization continua, in general agreement with an atomlike model.^{27,28} More recently, Child and Jungen have applied multichannel quantum defect theory (MQDT) to photoexcitation of asymmetric tops and performed numerical calculations for near-threshold ionization H_2O ($1b_1$)^{−1}.²⁹ In these calculations, the authors assumed only $d \leftarrow p$ excitations from which they were able to obtain a reasonable assignment for the high resolution H_2O photoionization spectrum obtained by Page *et al.*³⁰ Child and Jungen also showed that $l=\text{even}$ photoexcitation leads only to type c rotational transitions, for which $\Delta K_a=\text{odd}$ and $\Delta K_c=\text{even}$.

The association of type c transitions with $l=0$ and 2 continua is a general consequence of parity selection rules as illustrated for H_2O photoionization in Fig. 1. In this figure, the lowest rotational levels of the neutral $\tilde{X}^1A_1$ and ground $\tilde{X}^2B_1$ ionic states are shown along with their $|NK_aK_c\rangle$ assignments, rovibronic symmetries (Γ_{evr}) and parities

(p_{evr}).¹⁶ The symmetries are appropriate to a near-prolate top ($I_a < I_b \sim I_c$) with $a=y$, $b=z$, and $c=x$ (representation II of Zare).³¹ The ion levels may couple to an $l=\text{odd}$ or even angular momentum component of the photoelectron (shown as o and e) to give a complete Hund's case (d) parity ($p_{\text{evr}l}$). Using the general dipole selection rule for parity, $\oplus \leftrightarrow \oplus$, we find that $l=\text{odd}$ continua accompany type a transitions ($\Delta K_a=\text{even}$ and $\Delta K_c=\text{odd}$) and $l=\text{even}$ continua are associated with type c transitions, as noted above. Type b transitions, with both ΔK_a and ΔK_c odd or even, are strictly forbidden by nuclear spin statistics. A similar diagram describes H_2S photoionization, although the neutral and cation are closer to oblate tops.

The parity selection rules extracted from Fig. 1 have also been derived by Lee *et al.* through the use of Eq. (10), and general symmetry properties of asymmetric tops.^{2,3} Specifically, they find

$$\Delta K_a + l = \text{odd}, \quad (12)$$

which summarizes the $l=\text{odd}$ and $l=\text{even}$ parity restrictions for type a and type c transitions found above. Furthermore, they use Eq. (11) to show that $\Delta K_a + \Delta K_c = \text{odd}$. The latter indicates that both type a and type c transitions are dipole allowed, whereas type b transitions are forbidden independent of nuclear symmetry constraints. It is important to note that the type(s) of allowed transitions, e.g., type a , are specific to the asymmetric top case being studied. For formaldehyde, which is a near-prolate symmetric top ($I_a \ll I_b \sim I_c$), the C_2 axis is now identified with the a ($=z$) top axis. In this case, the rovibronic symmetries (Γ_{evr}) and level structure differ significantly from that in Fig. 1, although the parities for any $|NK_aK_c\rangle$ state are the same. To see how this affects which rotational transitions are allowed, we use Eq. (11) to determine the allowed values of K_η which corresponds to K_a in H_2CO . Dipole-induced photoionization from the outer $2b_2$ molecular orbital leads to ka_1 , ka_2 , and kb_2 ionization continua which, combined with the symmetries of the dipole operator in C_{2v} symmetry ($a_1 \rightarrow \mu=0$, $b_2 \rightarrow \mu=\pm 1$), gives $\Delta K_a=\text{odd}$. Consequently, only type c and type b ($\Delta K_a=\text{odd}$ and $\Delta K_c=\text{odd}$) ionization transitions are permitted, the latter being forbidden in H_2O and H_2S . The other type b transitions with $\Delta K_a=\text{even}$ and $\Delta K_c=\text{even}$ are forbidden. Parity selection rules, which are invariant to top classification, can now be summarized as $\Delta K_c + l = \text{even}$, in which type c and type b transitions remain coupled to $l=\text{even}$ and $l=\text{odd}$ continua, respectively.

1. H_2O and H_2S

Both the measured ZEKE-PFI and calculated threshold spectra for the (000) level of H_2O^+ (Fig. 1 of Ref. 2) exhibit strong type c rotational transitions with a number of weaker yet well isolated lines which can be assigned to type a transitions, e.g., $0_{00} \leftarrow 1_{01}$. According to the parity selection rule,^{2,3} these type a transitions arise from odd (almost pure p at threshold energies) wave contributions to the photoelectron matrix elements. These p waves of the ka_1 and kb_1 continua are entirely molecular in origin, since photoionization of the $1b_1$ orbital with its almost pure p (99.7%) character should lead only to s and d (even) waves in an atom-

iclike picture. The ka_2 continuum makes almost no contribution to these type a transitions, since its p wave is forbidden and f or higher odd waves are negligible.^{2,3}

The origin of type a transitions is not due to an inadequate description of the ground state, but results from np – nd Rydberg series interactions induced by the small, but finite anisotropy of the H_2X^+ core potential. At close range where the body-fixed C_{2v} symmetry components are well defined, the np and nd Rydberg series of the same λ (a_1 or b_1) can mix since l is not a good quantum number. The subsequent evolution of the photoelectron wave function from short-range to long-range results in Rydberg or photoelectron orbitals with orbital angular momentum components that reflect the l -mixing interactions at close range. Here this process results in p final waves with nonzero oscillator strength. This l -uncoupling process is one-electron in nature and the p – d interactions are simply a consequence of the electron ion–core interactions induced by the anisotropic core potential.

As noted earlier, Child and Jungen included only $d \leftarrow p$ excitations and thereby predicted that the rotationally resolved photoelectron spectrum would only include type c transitions as required by parity.²⁹ In a subsequent paper, Gilbert and Child proposed that the “anomalous” type a transitions could be explained by introducing a dipole-induced mixing between the strongly allowed nd series at high- n and “forbidden,” isoenergetic np levels converging to higher rotational limits.³² In their model, the zero-field dipole-mixing would lead to observable type a transitions via forced autoionization.^{32,33} The fact that these type a transitions are well accounted for on the basis of Hartree–Fock molecular photoelectron orbitals which correctly describe the angular momentum coupling inherent in such orbitals indicates that forced autoionization is not responsible for the appearance of type a lines. However, the MQDT approach to np – nd interactions mediated by long range dipolar coupling is quite appropriate. The nonzero dipole moment of H_2O^+ is simply a long range manifestation of the anisotropy of the cation potential. The essential physics is contained in both the Hartree–Fock and MQDT approaches and the H_2O example highlights the multichannel nature of molecular photoionization.

The rotationally resolved ZEKE-PFI spectrum for H_2S is similar to H_2O in that both type c and type a transitions are observed, however, the latter are significantly weaker.⁴ This result is readily attributed to the more massive sulfur atom, which causes the center of mass and center of charge to be more nearly coincident in H_2S^+ . Consequently, the molecular ion core potential is more spherical in nature and photoejection into kp continua is even less likely. *Ab initio* calculations confirm the more atomic nature of H_2S photoionization.⁵ Theoretical calculations show that the type a (odd wave contributions)/type c (even wave contributions) intensity ratios change from about 1:3 for H_2O to 1:14 for H_2S . In fact, these type a to type c intensity ratios in the photoelectron spectra of H_2O and H_2S correlate quite well with the dipole moments of the corresponding cations, i.e., $\mu_{H_2O^+} = -0.86$ a.u. and $\mu_{H_2S^+} = -0.51$ a.u. calculated with origin at the center of mass. This correlation is reason-

FIG. 2. Rotationally resolved threshold photoelectron spectrum for single-photon ionization out of the $2b_2$ orbital of H_2CO ; (a) experimental ZEKE-PFI spectrum and (b) *ab initio* calculation of the threshold photoelectron spectrum using a photoelectron kinetic energy of 50 meV and assuming a ground state rotational temperature of 7 K. Rotational levels are labeled by the total core angular momentum (exclusive of spin) and its a and c axis projections, i.e., $N_{K_a K_c}^+ \leftarrow J_{K_a K_c}''$. The upper labels for each ground state ladder correspond to type b transitions and the lower labels to type c transitions (see the text).

able since a body-fixed multipole expansion reflects the non-atomic-like character of the molecular ion core potential. The dipole component of this potential couples partial waves (l) differing by ± 1 and is the leading term of this expansion.

2. H_2CO

The one-photon ZEKE-PFI spectrum for the $\tilde{X}^2B_2(000)$ ground ionic state of H_2CO is shown in the upper panel of Fig. 2. Unlike H_2O and H_2S , the rotational spacings of H_2CO are determined mainly by the A rotational constant which is ~ 9 times larger than the B and C constants.³⁴ Consequently, the allowed type c and type b transitions of the same K_a but different K_c have nearly the same energy which results in considerable spectral congestion. Analysis of the rotational structure was also hampered by the fact that the rotational constants of the H_2CO^+ cation have not been determined by high-resolution methods. These were obtained from spectral simulations of the ZEKE-PFI spectrum using rotational constants derived from an *ab initio* electronic structure calculation of the H_2CO^+ geometry as initial estimates.³⁵ Further refinement resulted in the “best fit” rotational constants shown in Table I. These rotational constants were used to construct the calculated threshold photoelectron spectrum shown in the bottom frame of Fig. 2.

TABLE I. Rotational constants for H_2CO^+ cation.

Rotational axis	Rotational constant (cm^{-1}) ^a
A	8.875(3)
B	1.31 (1)
C	1.14 (1)

^aValues in parenthesis give the uncertainty in the last significant figure.

Both the simulations and the *ab initio* calculations indicate a ground state rotational temperature of ~ 7 K. The calculation is based on a photoelectron kinetic energy of 50 meV and uses a Gaussian detection function with a 1.8 cm^{-1} line width (FWHM).

The calculated threshold spectrum is in good agreement with ZEKE-PFI data and allows a breakdown of the separate contributions of type *c* and type *b* transitions which cannot be experimentally resolved. Figure 3 shows the calculated threshold photoelectron spectra for the individual type *c* [Fig. 3(a)] and type *b* [Fig. 3(b)] transitions of Fig. 2 for single-photon ionization of the $2b_2$ orbital of the ground state of H_2CO . Furthermore, our calculated spectra show a total intensity for type *b* transitions about twice as large as that for type *c* transitions. The relatively intense type *c* transitions (even wave contributions) cannot be accounted for on the basis of atomiclike propensity rules since the $2b_2$ orbital of the H_2CO has 4.81% *p*, 80.00% *d*, 3.69% *f*, 9.11% *g*, 1.52% *h* character. The mostly even wave character of the $2b_2$ or-

FIG. 3. Calculated photoelectron spectra for the (a) type *c* and (b) type *b* transitions of Fig. 2(b) for single-photon ionization of the $2b_2$ orbital of the $\tilde{X}^1A_1$ ground state of jet-cooled H_2CO . The type *b* to type *c* intensity ratio is about 1.9.

bital would be expected to lead to dominant odd partial wave contributions to the photoelectron matrix elements and, hence, to dominant type *b* transitions. This unexpected contribution from even partial waves of the photoelectron matrix element is molecular in origin and arises from strong *l* mixing due to the nonspherical molecular ion potential. The large dipole moment of H_2CO^+ ($\mu=0.95$ a.u.) is consistent with this highly anisotropic potential. In this regard, ionization of the $2b_2$ orbital of H_2CO is similar to that of the 2π orbital of NO which is also *d* type in character.³⁶ For the latter, *ab initio* calculations show that $(2\pi^*)^{-1}$ threshold photoionization results in a wide partial wave distribution with contributions from both *l*=even and *l*=odd continua.

B. Symmetric tops: CH_3

The methyl radical and cation are oblate symmetric tops, belonging to the D_{3h} molecular point group. Dipole-allowed transitions from the X^2A_2'' ground state of CH_3 occur to final states [ion core ($1A_1'$) + photoelectron] of A_1' ("parallel" transition) and E'' ("perpendicular" transition) overall symmetry. These short-range states correspond to dominant photoelectron continuum channels with ksa_1' , kda_1' , and kde'' symmetry, respectively. Transitions to *p*-type (*l*=1) continua, which transform as a_2'' and e' , are dipole forbidden. Since the a_2'' orbital is essentially an out-of-plane $2p$ orbital localized on the central carbon atom, these allowed final states are consistent with atomic selection rules ($\Delta l = \pm 1$). Furthermore, the center of charge and center of mass coincide for the CH_3^+ cation core and this nearly spherical potential (zero dipole moment) should result in highly atomiclike photoionization.

The rotationally resolved ZEKE-PFI spectrum for the methyl radical is shown in the upper panel of Fig. 4. Methyl radicals were produced by supersonic-jet flash pyrolysis of azomethane, CH_3NNCH_3 , as described elsewhere.⁷ The rotational structure is quite similar to that observed for the bound-bound β , $\delta \leftarrow X$ bands in CH_3 and CD_3 characterized by $\Delta K=0$ electronic transitions with simple *P*, *Q*, and *R* ($\Delta N = -1, 0, +1$) branches reminiscent of a diatomic molecule.³⁷ Due to the similarity of the ground and excited state structures, each branch line is comprised of many closely spaced $\Delta K=0$ subbands.^{37,38}

The bottom frame of Fig. 4 gives the calculated threshold photoelectron spectrum for single-photon ionization out of the a_2'' orbital of CH_3 assuming a ground state rotational temperature of 250 K. The dominant $\Delta K=0$ structure is clearly reproduced with $\Delta K = \pm 1$ transitions predicted to be too weak to be observed. The relative branch intensities are in reasonable agreement with experiment with some notable exceptions at lower energy. The anomalously high intensity observed for the *O*(6) branch line is most likely a result of near-resonant rotational autoionization.^{7,39}

The observation of dominant $\Delta K=0$ transitions for photoionization of CH_3 suggests that ka_1' parallel continua dominate at threshold. Application of Eqs. (6) and (11), however, shows that both ka_1' and ke'' continua can lead to $\Delta K=0$ transitions; values of the dipole-allowed combinations of μ and λ for $ks(l=0)$ and $kd(l=2)$ partial waves

FIG. 4. Rotationally resolved threshold photoelectron spectrum for single-photon ionization out of the $1a_2''$ orbital of CH_3 ; (a) measured ZEKE-PFI spectrum and (b) *ab initio* calculation of the threshold photoelectron spectrum using a photoelectron kinetic energy of 50 meV, an FWHM of 2.5 cm^{-1} , and assuming a ground state rotational temperature of 250 K. The rotational branches are labeled according to $\Delta N = N^+ - N''$ and where the branch ladders are numbered by N'' . All the rotational transitions of significant intensity have $\Delta K = 0$ (see the text).

can be readily obtained from the D_{3h} character table. For photoionization to ka_1' continua one obtains $\mu = \lambda = 0$, and for ke'' one obtains $\mu = \lambda = \pm 1$. This yields the result that $\Delta K = 0, \pm 2$. Indeed, our calculations reveal that $\Delta K = 0$ are the dominant transitions (up to 95%) and the $|\Delta K| = 2$ (not labeled) transitions are substantially weaker. Transitions involving $\Delta K = \text{odd}$ are also dipole allowed, however, their intensities are even weaker and they do not appear in the spectrum. The latter are associated with odd values of $\mu + \lambda$ which originate from $kf(l=3)$ components of the continuum (kfa_1' , $\lambda = \pm 3$ or kfe'' , $\lambda = \pm 2$).⁴⁰ These, in turn, may result from $g(l_0=4, \lambda_0=\pm 3)$ wave contributions to the $1a_2''$ ground state orbital. The $1a_2''$ orbital is calculated to have almost pure p character (99.9%), so that ionization transitions to continua with $l \geq 3$ are expected to be very weak. Consequently, dipole transitions between the neutral and final (electron plus ion core) states are dominated by $l = \text{even}$, confirming the $(s,d) \leftarrow p$ atomic nature of $\text{CH}_3(a_2'')^{-1}$ photoionization.

The physical significance of these results is that (1) the small anisotropy of the CH_3^+ core potential does not induce strong mixing of $l = \text{even}$ and $l = \text{odd}$ partial waves at short range; (2) the classification of particular bound-to-continuum transitions as parallel or perpendicular is inappropriate. The latter is a result of l uncoupling of the continuum as the

photoelectron final states evolve from short to long range. In this fragmentation process (frame transformation), the molecular symmetry orbitals (ka_1' and ke'') do not have a one-to-one correspondence with a specific photoelectron angular momentum (l) at long range. An analogous "decomposition" occurs for the asymmetric top molecules discussed earlier, where the body-fixed photoelectron symmetry orbitals contribute to all three types (a, b, c) of observed bound-to-continuum rotational transitions.⁴¹

Although the continuum channels cannot be separated according to parallel and perpendicular transitions, it is still possible to use these characterizations with respect to the core electronic angular momentum. Specifically, it is possible to predict the even or odd nature of ΔK_η by determining the effect of a $C_{\eta(z)}$ rotation on the point group representation of the core electronic angular momentum. In the case of methyl, both the neutral (X^2A_2') and the ionic ($1A_1'$) core states remain unchanged upon rotation about the C_3 axis, so that only $\Delta K = \text{even}$ transitions are expected. This result is in agreement with that obtained by application of $\Delta K = \mu + \lambda$. Generalizing these arguments, we classify photoionization transitions as parallel ($\Delta K = \text{even}$) or perpendicular ($\Delta K = \text{odd}$) according to the change in the projection of the core electronic angular momentum on the axis of highest symmetry (K_η). The latter is obtained from point group character tables which indicate the effect of rotation about the $C_{\eta(z)}$ axis.

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