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Angular and internal state distributions of H_2^+ generated by (2 + 1) resonance enhanced multiphoton ionization of H₂ using time-of-flight mass spectrometry

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We report direct measurement of the anisotropy parameter β for the angular distribution of the photoelectron and photoion in (2 + 1) resonance enhanced multiphoton ionization process of H₂ X ${}^{1}\Sigma_{g}^{+}$ (v = 0, J = 0) molecules through the intermediate H₂ E,F ${}^{1}\Sigma_{g}^{+}$ (v' = 0, J' = 0) level $(\lambda = 201.684 \text{ nm})$ using a time-of-flight mass spectrometer. The time-of-flight spectra were recorded as the direction of polarization of the ionizing laser was varied with respect to the flight axis of the H₂ molecular beam and were fitted to an angular distribution in an appropriately rotated coordinate system with the z-axis oriented along the time-of-flight axis. The anisotropy parameter β was found to be 1.72 ± 0.13 by fitting the time-of-flight spectra and agreed with previous measurements. Using secondary ionization with a delayed laser pulse of different wavelength, we also determined the vibrational energy distribution of the ions, showing that $98\% \pm 4\%$ of the ions are generated in their ground vibrational state, in agreement with the calculated Franck-Condon factors between the H₂ E,F ${}^{1}\Sigma_{q}^{+}$ (v' = 0) and H₂⁺ X ${}^{1}\Sigma_{q}^{+}$ (v'') vibrational levels. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4952759]

I. PHOTOFRAGMENT ANGULAR DISTRIBUTION

For one-photon ionization of unpolarized molecules using plane polarized light, the angular distribution of the photoion as well as the photoelectron is constrained by symmetry to have the form

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)], \qquad (1)$$

where σ is the total cross section for photoionization, θ is the angle measured with respect to the electric field of the light, and $P_2(\cos \theta) = (3\cos^2 \theta - 1)/2$ is the second-order Legendre polynomial.^{1,2} Here β is the asymmetry parameter, which ranges from -1 where $I(\theta) \propto \sin^2 \theta$ to 2 where $I(\theta) \propto \cos^2 \theta$.

For a given polarization direction Θ of the laser with respect to the time-of-flight (TOF) axis, the angular distribution in Eq. (1) can be related to the photoion recoil speed distribution along the flight axis of a time-of-flight spectrometer. Therefore, by measuring the photoion velocity distribution for different polarization directions, it is possible, in principle, to deconvolute the spectrum and find the angular distribution of both the photoion and photoelectron. It is this seldom used approach^{3,4} that we employ to determine the photoionization anisotropy in the (2 + 1) resonance-enhanced multiphoton ionization (REMPI) of H_2 in the (v = 0, J = 0) vibrational–rotational level of the X ${}^{1}\Sigma_{g}^{+}$ ground state via the H₂ E,F ${}^{1}\Sigma_{\rho}^{+}$ (v' = 0, J' = 0) level to the ionization continuum. See Fig. 1, adapted from previous theoretical studies,⁵ for potential energy curves of these three states.

In order to measure perturbations in the time-of-flight distribution caused by the recoil of the photoelectron, we need to start with a well-defined velocity distribution in the neutral molecules. For this purpose, we employ a supersonic beam of neutral H₂. The supersonic beam of H₂ molecules has a narrow

velocity distribution around 2800 m/s which is fairly Gaussian having a full width at half maximum of approximately 200 m/s. As a result of ionization, the velocity distribution is perturbed by the recoil of the escaping photoelectron whose angular distribution is given in Eq. (1). The photon energy in excess of what is needed to cause ionization is partitioned between the ion and electron using the conservation of momentum. The velocity distribution of H_2^+ along the axis of detection, designated as the z' axis, is modified by the recoil of the ejected electron and can be expressed by

$$F(v) \propto \int g(v - v_e \cos \theta') h(\theta', \phi') d\Omega'.$$
 (2)

The function g represents the molecular beam longitudinal velocity distribution along the beam axis, which is coincident with the detection axis z', and v_e represents the maximum recoil speed of the photoelectron. Normally, a slightly skewed distribution g can be expressed⁶ by

$$g = (v - v_e \cos \theta')^2 \exp\{-[(v - v_e \cos \theta' - v_o)/\Delta v]^2\},$$
(3)

where Δv is the longitudinal velocity spread, which is determined by the longitudinal temperature of the molecular beam, and v_o is the velocity for mass flow along z'. In Eq. (2), $h(\theta', \phi')$ is the probability of finding a recoil velocity v_e along (θ', ϕ') per unit solid angle about the detection axis z'.

The function $h(\theta', \phi')$ can be found in the following way. The photoelectron distribution $S(\theta, \phi)$ about the linearly polarized optical field E along the quantization axis z is given by Eq. (1). If E is oriented at an angle Θ with respect to the detection axis z', then $h(\theta', \phi')$ can be found from the transformation property of the Legendre polynomial P_2 under rotation of the coordinate system that brings z to z'. Thus, under rotation $S(\theta, \phi) = 1 + \beta P_2(\cos \theta)$ transforms into

$$h(\theta',\phi') = 1 + \sqrt{4\pi/5} \beta \sum_{m=-2}^{2} D_{0m}^{2}(0,\Theta,0) Y_{2m}(\theta',\phi')$$

= 1 + $\sqrt{4\pi/5} \beta \{P_{2}(\cos\Theta)Y_{20}(\theta',\phi') + \sqrt{6}\cos(\Theta/2)\cos\Theta\sin(\Theta/2) [Y_{2-1}(\theta',\phi') - Y_{21}(\theta',\phi')] + \sqrt{6}\cos(\Theta/2)^{2}\sin(\Theta/2)^{2} [Y_{22}(\theta',\phi') + Y_{2-2}(\theta',\phi')]\},$ (4)

where $D_{0m}^2(0,\Theta,0)$ is the Wigner rotation matrix element⁷ for the second-rank spherical harmonic $Y_{2m}(\theta, \phi)$. The velocity distribution for the recoiling ions is found by inserting Eqs. (3) and (4) into Eq. (2) and integrating over the azimuthal angle ϕ' about the detection axis z',

$$F(v) \propto \int_0^{\pi} (v - v_e \cos \theta')^2 \exp\{-[(v - v_e \cos \theta' - v_0)/\Delta v]^2\} \times [1 + \beta P_2(\cos \Theta) P_2(\cos \theta')] \sin \theta' d\theta'.$$
(5)

Using a linear relation between the time-of-flight and velocity along the detection axis of the time-of-flight spectrometer, the velocity distribution in Eq. (5) can be converted into the arrival time distribution,

$$f(\tau) \propto \int_{0}^{\pi} (\tau - \alpha \cos \theta')^{2} \exp\{-[(\tau - \tau_{o} - \alpha \cos \theta')/\Delta\tau]^{2}\} \times [1 + \beta P_{2}(\cos \Theta)P_{2}(\cos \theta')] \sin \theta' d\theta'.$$
(6)

Here, τ_o corresponds to the time-of-flight (TOF) of the peak velocity, and $\Delta \tau$ is the width of the distribution in the absence of photoelectron recoil. The parameter α is determined by the



FIG. 1. Adiabatic potentials for the H₂ X ${}^{1}\Sigma_{g}^{+}$, H₂ E,F ${}^{1}\Sigma_{g}^{+}$, and H₂⁺ X ${}^{1}\Sigma_{g}^{+}$. It is clear that the minima of the potential wells for the H₂ E,F ${}^{1}\Sigma_{p}^{+}$ and $H_2^+ X \Sigma_q^+$ states line up extremely well, which indicates that the ions should be generated in the vibrational ground state. This figure is adapted from previous theoretical calculations.

product of the maximum recoil speed of the photoelectron and the resolution of the TOF mass spectrometer.

II. ANISOTROPY PARAMETER FROM FITTING TIME-OF-FLIGHT SPECTRA

A supersonically expanded and collimated beam of H₂ molecules was generated using a Series 9 General Valve (Parker Precision Fluidics) with an orifice diameter of 0.75 mm and a stagnation pressure of 3 atm. The valve was operated using current pulses of 140 μ s duration and expanded into a chamber whose pressure was 10 μ Torr under the steady-state operating condition. It was then collimated by a skimmer (Beam Dynamics) with an orifice diameter of 2 mm which generated a molecular beam of H_2 in the (v = 0, J = 0) level of its ground electronic state X ${}^{1}\Sigma_{g}^{+}$, which was then ionized via the two-photon resonant (v' = 0, J' = 0) level of the E,F ${}^{1}\Sigma_{p}^{+}$ state using linearly polarized VUV laser pulses at 201.63 nm. The VUV laser pulse was focused using a 30 cm focal length fused silica lens and intersected the molecular beam transversely. Tunable VUV pulses were obtained by using two different β -barium borate (BBO) crystals in sequence to generate the third harmonic of a tunable pulsed dye laser (ND 6000, Continuum Lasers, Inc.) operating at 20 Hz. The resonant line used was found at a VUV wavelength of 201.648 nm in vacuum. The (2 + 1) REMPI generated ions were collected on a pair of 12 cm diameter multichannel plate detectors located at the end of a 29 cm long time-offlight mass spectrometer. Figure 2 shows the TOF spectra of the H_2^+ ions for different polarization directions Θ of the linearly polarized VUV laser pulses defined with respect to the detection axis. The polarization direction of the VUV laser was fixed by combined rotation of a half-wave retarder and the transmission axis of a α -BBO Glan polarizer which has an extinction ratio better than (1:1000). In our experiment, the H_2^+ ions are not rotationally resolved. For each H_2^+ TOF spectrum shown in Fig. 2, approximately 5000 data points were collected over a time period of several hours under the condition of less than a single count on our MCP per laser pulse, which is coupled to a position-sensitive delay line anode detector (model DLD-120, RoentDek Handels GmbH, Kelkheim, Germany).

Figure 2 shows the fitted time-of-flight spectra as a function of probe laser polarization. For the polarization direction parallel to the detection axis ($\Theta = 0^{\circ}$), the recoil effect is most pronounced, and the distribution separates into two peaks corresponding to two possible directions of the ejected electron travelling parallel or anti-parallel to the detection axis. This behavior is clearly evidenced in the top panel Fig. 2(a). Eq. (6) was fitted to the TOF spectra of Fig. 2



FIG. 2. Time-of-flight spectra of the H₂⁺ ion for (a) $\Theta = 0^{\circ}$; (b) $\Theta = 30^{\circ}$; (c) $\Theta = 60^{\circ}$; and (d) $\Theta = 90^{\circ}$. The green curves are fits to the blue data points, based on the fitting for $\Theta = 0^{\circ}$ using Eq. (6) with $\alpha = 8.3$ and $\beta = 1.72$.

using the "NonlinearModelFit" program of Mathematica,⁸ which produced a value of $\beta = 1.72 \pm 0.13$. The R^2 value of the fit was better than 0.99. This large value of the anisotropy parameter corresponds to a highly polarized ejection of the electron in the direction of the optical field.

Figures 2(b)-2(d) show the TOF spectra of H_2^+ for the polarization directions $\Theta = 30^\circ$, 60° , and 90° of the optical field relative to the detection axis. With decreasing recoil along the detection axis, the two peaks of the velocity distribution draw closer together and ultimately form a single peak for $\Theta = 90^{\circ}$. Figures 2(b)–2(d) are fitted using Eq. (6) with the value of β found from fitting Fig. 2(a) yielding a satisfactory fit with R^2 values in excess of 0.99, which provides high confidence for the asymmetry parameter we report. These near-unity R^2 values also validate that Eq. (1) gives the exact form of the photoelectron angular distribution for unpolarized or isotropic molecules in one-photon ionization processes. We point out that a narrow two-photon resonance ~10 MHz of the E,F ${}^{1}\Sigma_{\rho}^{+}$ state combined with a narrow laser linewidth causes insignificant ($\Delta v_e/v_e < 0.01\%$) broadening for the recoil speed of the ion. Figure 3 presents a three-dimensional plot of the photoelectron angular distribution given in Eq. (1) using $\beta = 1.72.$

The value of $\beta = 1.72 \pm 0.13$ found here matches with the previously measured value using single photon excitation from the unpolarized ground vibrational state of the H₂ molecule.⁹



FIG. 3. Three-dimensional plot of the photoelectron angular distribution for the asymmetry parameter $\beta = 1.72$.

The photoionization process considered here is (2 + 1)REMPI that occurs via the two-photon resonant (v' = 0, J' = 0) E,F ${}^{1}\Sigma_{g}^{+}$ excited state. The (2 + 1) REMPI is a cascade process in which the final step is the single photon ionization from the two-photon resonant (v' = 0, J' = 0) E,F ${}^{1}\Sigma_{g}^{+}$ excited state. Because molecules in the two-photon resonant state are isotropic and have the same parity and angular momentum as molecules in the (v = 0, J = 0) level of the H₂ ground state, it is not surprising that (2 + 1) REMPI via the (v' = 0, J' = 0) level of the E,F ${}^{1}\Sigma_{g}^{+}$ state will have the same characteristic angular distribution as the direct photoionization from the unpolarized ground vibrational level of the ground electronic state.

These fits also generated a value of the width parameter $\Delta \tau = 3.58 \pm 0.18$ ns, which corresponds to a spread in the velocity distribution of 123 ± 6.2 m/s. This fitting parameter $\Delta \tau$ gives us directly the velocity distribution of our molecular beam pre-ionization. Using a value of $C_p/C_v = 1.405$ and the ratio between the beam speed and the width of the speed distribution, we calculate¹⁰ the translational temperature to be approximately 2 K.

III. DETERMINATION OF ION VIBRATIONAL DISTRIBUTION

The conservation of energy and linear momentum allows us to relate the ion internal energy to the recoil momentum as follows:

$$h\nu - IE = \frac{p^2}{2m_{H_2^+}} + \frac{p^2}{2m_e} + E_{int},$$
(7)

where hv is the ionizing photon energy, *IE* is the ionization energy for H₂ molecules in the E,F ${}^{1}\Sigma_{g}^{+}(v'=0, J'=0)$ level (approximately 3.3 eV), *p* is the recoil momentum, m_i is the mass of the recoiling particle *i*, and E_{int} is the internal energy of the ion. The fitting of the time-of-flight spectra generates α parameters which give the time, in nanoseconds, corresponding to the recoil speed in the center of mass frame of the molecule for a given ionizing photon energy. For the wavelength used in (2 + 1) REMPI, there is approximately 3 eV of energy available after ionizing the molecule. In the case of the (2 + 1) REMPI wavelength, this energy is sufficient to populate H₂⁺ vibrational states up to v⁺ = 11. When we attempted to fit the time-of-flight data using a sum



FIG. 4. Time-of-flight spectra for ionizing light at (a) 201.658 nm (b) 233.077 nm, and (c) 266.112 nm. The green curves are fits of the blue data points using Eq. (6) with $\Theta = 0^{\circ}$ and $\beta = 1.72$. These plots were fitted with a 99% confidence level.

of distributions each with a different α parameter, the fitting would not converge. On the other hand, fittings using only a single recoil speed had very high R² values. These two facts suggest that only one H₂⁺ vibrational state is populated by the ionization process. In order to determine which vibrational state was populated, we need to relate our single-valued α parameter to a recoil speed, which required a time to velocity calibration.

To calibrate our instrument and in the process determine the vibrational energy distribution of the ion, we have employed a two-color secondary ionization technique using time delayed pulses. In the first step of the process the so-called "primary" light pulse of 201.684 nm, which was generated in the same manner detailed above, was used to excite the molecule from the ground H₂ X ${}^{1}\Sigma_{g}^{+}$ (v = 0, J = 0) level to the two-photon excited H₂ E,F ${}^{1}\Sigma_{g}^{+}$ (v' = 0, J' = 0) level. A delayed second laser pulse with wavelength of 233 nm or 266 nm was then used to ionize the H₂ molecule from the two-photon resonant H₂ E,F ${}^{1}\Sigma_{g}^{+}$ (v' = 0, J' = 0) level using single-photon excitation. Both the primary and secondary pulses are polarized along the time-of-flight axis. The 233 nm laser pulse was generated by sum frequency mixing of 355 nm and 680 nm pulses in a α -BBO crystal. The 355 nm pulse was derived from the third harmonic of a second Nd:YAG laser which was time locked with the Nd:YAG laser used to generate the primary laser pulse. The 680 nm laser pulse was derived from a seeded pulsed dye amplifier which was pumped by the second harmonic of the same Nd:YAG laser which was used to generate the 355 nm light. The pulse at 266 nm was formed by doubling the second harmonic of the second Nd:YAG in a KTP crystal. The secondary laser pulse was focused downstream from the primary laser pulse using a 40 cm focal length lens and both secondary pulses (233 nm and 266 nm) had sufficiently low intensity to ensure single-proton coupling to the continuum. The extraordinarily long lifetime (in excess of 500 ns) of the H₂ E,F ${}^{1}\Sigma_{g}^{+}$ state allowed us to separate the bound-bound two-photon transition stimulated by the 201.684 nm light pulse from the bound-free transition initiated by the 233 nm or 266 nm pulse. A time separation of 200-500 ns between the primary and secondary laser pulses was employed to ensure that there would be no temporal overlap between the ions generated by the primary

and secondary lasers. In order to verify that no ions were generated by off-resonant multiphoton ionization from the second laser pulse, the signal was observed to disappear when the two-photon resonant pulse was blocked. The time-of-flight spectra of the secondary ions were recorded under single hit conditions in the same manner detailed above for the (2 + 1)REMPI process. The time-of-flight spectra of the secondary ions were fitted using Eq. (6) and the same Mathematica program detailed above. The fitted spectra are shown in Fig. 4.

It is clear that as the ionizing wavelength is increased, the splitting between the two recoil peaks is also reduced as expected. For each wavelength which is used to ionize the H_2 molecules in the experiment hv - IE is large enough to populate the ionic vibrational levels up to at least $v^+ = 6$. For ionization using both 233 nm and 266 nm, like 202 nm, the fits gave very high agreement ($R^2 > 0.99$) using only a single value of α , rather than a sum of distributions each using a different α parameter. These fitted α parameters are shown in Fig. 5, plotted against recoil speeds calculated considering $v^+ = 0$, 1, and 2 vibrational states of the ion. The recoil speeds were calculated using Eq. (7) and previously calculated internal energies of the H_2^+ ion.¹¹ Figure 5 shows that only the fitted line corresponding to $v^+ = 0$ passes through the origin of our speed vs time plot. Clearly, an α of 0 ns should correspond to a recoil velocity of 0 m/s, so this proves that our ions are generated almost exclusively in $v^+ = 0$. Using



FIG. 5. Fitting parameter α generated from time-of-flight data using different ionizing wavelengths plotted against the calculated recoil speed as a function of ion vibrational level at that wavelength. $\alpha = 5.97$ ns, 6.85 ns, and 8.3 ns correspond to spectra generated by 266 nm, 233 nm, and 202 nm, respectively. The solid blue line representing v⁺ = 0 clearly passes through the origin, showing that v⁺ = 0 is the level in which the photoions are generated.



FIG. 6. Image of the H_2^+ in a plane perpendicular to the detection axis for (a) $\Theta = 0^\circ$; and (b) $\Theta = 90^\circ$.

the error in the fitted parameter α , we are able to estimate the error in our assignment of the ion vibrational level. An error of ±0.15 ns in α allows us to estimate that 98% ± 4% of the H₂⁺ ions are formed in v⁺ = 0. This agrees with Chandler and Parker's previous measurements¹² showing that in (2 + 1) REMPI through the H₂ E,F ${}^{1}\Sigma_{g}^{+}$ state, H₂⁺ is generated in a single vibrational level.

To compare with the experimentally determined internal state distribution, Franck-Condon factors from the $H_2 E, F^{1}\Sigma_{g}^{+}$ (v' = 0, J' = 0) to the H_2^{+} vibrational levels were calculated using harmonic oscillator wave functions. For the low vibrational levels of interest, harmonic oscillator wave functions created using previous spectroscopic data¹³ should have good approximations. Because the ionized molecule is first excited to H₂ E,F ${}^{1}\Sigma_{p}^{+}$ (v' = 0, J' = 0), where the molecular vibrations are localized to the E well of the state,¹⁴ the transition is found to have nearly diagonal Franck-Condon factors with over 99% probability of finding the ion in its vibrational ground state. The diagonality is clearly shown by the nearly identical position of the potential minima of these two states as it can be seen in Fig. 1. Thus, our calculated Franck-Condon factors are in complete agreement with our experimental data indicated by the fitted blue line in Fig. 4 passing through the origin as previously discussed. These findings are a better match for the calculated Franck-Condon factors than previously published results¹⁴ measuring the photoelectron velocity distribution.

Figure 6 shows images of the H_2^+ ions generated by (2 + 1)REMPI with 202 nm light detected on the position-sensitive delay-line anode with light polarization angle (a) $\Theta = 0^{\circ}$ and (b) $\Theta = 90^{\circ}$, relative to the time-of-flight axis. The image plane is perpendicular to the detection axis. Thus, for $\Theta = 0^{\circ}$, the optical field is perpendicular to the image plane, and therefore cylindrical symmetry is expected about the detection axis as nearly evidenced in Fig. 6(a). The slight oblong image shape is caused by a finite depth of focus of the UV beam exciting the molecular beam. For $\Theta = 90^\circ$, the optical field lies in the image plane, and the cylindrical symmetry about the detection axis is lost as seen in Fig. 6(b). Figure 6(b) shows that for the polarization direction vertical to the detection axis, the image in Fig. 6(a) is split vertically by the recoil of the photoelectrons and separates by a vertical distance of 2.7 mm, corresponding to a recoil speed of 281 m/s. This is the speed that we expect for H_2^+ ions generated in $v^+ = 0$, which again agrees with our measurement of the ion vibrational level.

Although we have considered here a case of a purely isotropic molecule with J = 0, in the absence of saturation, the asymmetry parameter β found in this study can be used to describe the (2 + 1) REMPI for unpolarized rotational states with $J \neq 0$. The reason for this behavior is that (2 + 1) REMPI process involves one-photon ionization from the bound intermediate state.

Finally, it is worthwhile to emphasize both the generality and the limitations of this method for determining photofragment angular and internal energy distributions. For the recoil measurements to be effective, it is necessary for the recoil velocity to be comparable or greater than the spread in the target velocity. For photoionization, this condition limits the applicability of this method to light molecules and fast photoelectrons. Indeed, it seems that molecular hydrogen and its isotopomers are among the very few molecules that satisfy this condition without great efforts being made to narrow the target velocity. However, if this technique is applied to photodissociation, such as $AB^+ + h\nu \rightarrow A^+ + B$ or $A + B^+$, the kick on the detected ion can be readily measured. An example is the photodissociation of $I^- \cdot CH_3 I.^{15}$

IV. CONCLUDING REMARKS

Using a simple time-of-flight spectrometry technique, we have demonstrated direct measurement of the anisotropy parameter for the angular distribution of the (2 + 1) REMPI generated H_2^+ ions and associated photoelectrons. The value obtained by these measurements is in close agreement with a previously measured value of the anisotropy parameter in single-photon ionization of unpolarized H_2 molecules. The technique presented here is quite general and can be applied to describe the photofragmentation of light unpolarized molecules. For polarized molecules with axial symmetry, Eq. (6) can be generalized by including higher order Legendre polynomials.

In addition, by calibrating the recoil speed against the temporal splitting of the peaks in TOF spectra, we have determined that the vibrational energy distribution of the ion is sharply peaked which is in close agreement with the calculated Franck–Condon factor between the E,F state and the ionic state. As it is well known, the asymmetry parameter β provides information on the nature of the molecular orbitals from which photoionization occurs. Furthermore, these measurements will allow the deconvolution of ionization

effects from time-of-flight spectrometry data, allowing an increase in angular resolution in experiments such as state-to-state reaction dynamics.

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- ¹J. Cooper and R. N. Zare, J. Chem. Phys. **48**, 942 (1968); **49**, 4252 (1968).
- ²K. L. Reid, Annu. Rev. Phys. Chem. **54**, 397 (2003).
- ³R. L. Toomes, P. C. Samartzis, T. P. Rakitzis, and T. N. Kitsopoulos, Chem. Phys. **301**, 209 (2004).
- ⁴H. Kawamata, H. Kohguchi, T. Nishide, and T. Suzuki, J. Chem. Phys. **125**, 133312 (2006).
- ⁵U. Fantz and D. Wünderlich, At. Data Nucl. Data Tables **92**, 6 (2006).

- ⁶H. Haberland, U. Buck, and M. Tolle, Rev. Sci. Instrum. **56**, 1712 (1985).
- ⁷R. N. Zare, *Angular Momentum* (Wiley, New York, 1988).
 ⁸See https://www.wolfram.com/mathematica for modern technical computing.
- ⁹S. Southworth, W. D. Brewer, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, and D. A. Shirley, J. Electron Spectrosc. Relat. Phenom. **26**(1), 43 (1982).
- ¹⁰W. Christen, K. Rademann, and U. Even, J. Chem. Phys. **125**, 174307 (2006).
- ¹¹J. Ph. Karr and L. Hilico, J. Phys. B: At., Mol. Opt. Phys. 39, 2095 (2006).
- ¹²D. W. Chandler and D. H. Parker, in *Advances in Photochemistry*, edited by D. C. Neckers, D. H. Volman, and G. von Bünau (John Wiley and Sons, 1999).
- ¹³G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold Company, New York, NY, 1950).
- ¹⁴S. L. Anderson, G. C. Kubiak, and R. N. Zare, Chem. Phys. Lett. **105**, 1 (1984).
- ¹⁵D. M. Cyr, C. G. Bailey, D. Serxner, M. G. Scarton, and M. A. Johnson, J. Chem. Phys. **101**, 10507 (1994).