Photodissociation of long-range Rydberg molecules

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We present photodissociation of ultracold long-range Rydberg molecules as a tool to characterize their electronic properties. We photoassociate $^{39}$K$_2$ $^{37}$P molecules with highly entangled electronic and nuclear spins of the two bound atoms and quantify the entanglement by projection of the molecular state onto non-interacting atoms using radiofrequency photodissociation. By comparison of experimental photodissociation rates with theoretical predictions we further characterize the electronic and nuclear wavefunction of the photoassociated molecules. Based on the complete characterization of the formed long-range Rydberg molecules, we demonstrate a full hyperfine-spin flip of a free ground-state atom through the interaction with a Rydberg atom.

Photodissociation of cold molecules is a powerful tool, providing quantum control of the photofragments’ internal and translational state [1–3]. It has been used, e.g., to produce atoms and molecules with very low kinetic energy for high-resolution collision and spectroscopic studies [4, 5] and aligned molecular samples [6, 7], as well as beams of spin-polarized atoms [8, 9]. Photodissociation of very weakly bound ultracold molecules was used to probe interactions in highly-degenerate quantum gases [10–13]. Here we apply photodissociation to long-range Rydberg molecules (LRMs). LRM are bound states of a ground-state atom located within the orbit of a Rydberg electron, where the binding is provided by the Rydberg-electron–ground-state atom scattering interaction [14]. LRM have previously been studied by photoassociation (PA) spectroscopy [15–17] and radiofrequency (RF) spectroscopy [18], extracting, e.g., electron-atom scattering parameters from binding energies [19–21] and determining dipole moments [22, 23].

In this letter, we present photodissociation as a probe of electronic properties of LRM. As an exemplary system, we study LRM of $^{39}$K$_2$ with highly entangled spins of the Rydberg and ground-state atom, formed by photoassociation [24]. We photodissociate these molecules at the threshold of non-interacting atomic asymptotes by RF radiation, a process which projects the entangled electronic state onto an unperturbed basis of atomic states. This allows for (i) the control of the internal state of ground-state atoms through interaction with a Rydberg atom at large interatomic separations, and (ii) a tomographic characterization of the photoassociated LRM.

The electronic Hamiltonian of a LRM in the Born-Oppenheimer approximation (neglecting the hyperfine interaction of the Rydberg atom) is given by

$$H = H_0 + A_{\text{hfs}} \vec{s}_{\text{gs}} \cdot \vec{j}_{\text{gs}} + A_{\text{so}} \vec{l} \cdot \vec{s}_{\text{Ryd}} + \Delta V \vec{s}_{\text{Ryd}} \cdot \vec{s}_{\text{gs}} + \vec{V},$$

(1)

which includes $H_0$, the Coulomb interaction of the ion core with the Rydberg electron [25], the spin-orbit coupling of the Rydberg-electron spin $\vec{s}_{\text{Ryd}}$ and orbital angular momentum $\vec{l}$ to form $\vec{j}$ with a state-dependent constant $A_{\text{so}}$, and the hyperfine coupling between the electronic ($\vec{s}_{\text{gs}}$) and nuclear ($\vec{i}_{\text{gs}}$) spin of the ground-state atom to form $\vec{F}$ with the coupling constant $A_{\text{hfs}}$. The binding Fermi-contact interaction $V_c$ between the Rydberg and the ground-state atom depends on the total electronic spin $S$ of the collision complex [19, 26]. In Eq. (1), $V_c$ is split into a spin-dependent part $\Delta V = V_c^3 - V_c^1$ and a spin-independent part $\bar{V} = \frac{3}{4} V_c^3 + \frac{1}{4} V_c^1$, where superscripts 1 and 3 refer to the scattering in singlet and triplet channels, respectively.

The Hamiltonian (1) conserves the quantity

$$\Omega = m_i + m_{s_{\text{Ryd}}} + m_{s_{\text{gs}}} + m_i = m_j + m_F,$$

(2)

which is the projection of the total angular momentum onto the internuclear axis (chosen along the $z$-axis), and is commonly represented in a basis comprising direct-
product states of the Rydberg atom and ground-state atom \(|n, l, j, m_j⟩ |F, m_F⟩\) \[27, 28\]. Here, \(|n, l, j, m_j⟩\) denotes the state of the Rydberg atom and \(|F, m_F⟩\) denotes the hyperfine state of the \(4^2S_{1/2}\) ground state of \(^{39}\)K. For clarity we will omit \(m_j\) and \(m_F\) in the following. As commonly done in the treatment of LRM, we consider Rydberg and ground-state atom as distinguishable particles \[14, 22\].

The spin-dependent term \(\Delta V \vec{s}_{\text{Ryd}} \cdot \vec{s}_{\text{gs}}\) in Eq. (1) takes the form of the Heisenberg-Dirac Hamiltonian for the two-electron exchange interaction \(29\), which creates entanglement of the hyperfine state of the ground-state atom \(F\) and the spin-orbit state \(j\) of the Rydberg atom \[24\]. By fortuitous coincidence, at \(n = 37\), the fine-structure splitting of the \(^{39}\)K \(^{n2P}_{j}\) Rydberg state is almost degenerate with the ground-state hyperfine splitting of \(^{39}\)K (456.2 MHz and 461.7 MHz, respectively) \[25\], and the entanglement may become especially large.

Fig. 2a depicts calculated potential-energy curves (PECs) for \(\Omega = 1/2\) states correlated to the nearly degenerate \(|37, 1, j⟩ |F⟩\) asymptotes (see Appendix A1). We label electronic states by approximate term symbols \(^3\Sigma^+\) (dark and light green), \(^1\Sigma^+\) (dark and light red), and \(\Pi\) (blue), where the superscript indicates if the binding results only from triplet (3) or singlet-triplet mixed scattering (1,3). Only in \(^3\Sigma^+\) states, \(F\) (the hyperfine state of the ground-state atom) is a good quantum number, whereas it is mixed in \(^1\Sigma^+\) states \[26\]. \(\Sigma\) and \(\Pi\) refer to states with and without \(m_1 = 0\) contributions, respectively (see Appendix A1). Because the electronic wavefunctions of \(|m_j⟩ > 0\) states have a nodal plane containing the internuclear axis, the scattering interaction in these states tends to zero in first order. Driving a \(\Sigma\) to \(\Pi\) transition in a LRM thus selectively switches off the scattering interaction by promoting the Rydberg electron to a spatial orbit with near-zero overlap with the ground-state atom.

The states \(|\phi⟩\) depicted in Fig. 2a exhibit almost exclusively \(|37, 1, 3/2⟩ |1⟩\) and \(|37, 1, 1/2⟩ |2⟩\) character. Their state vectors can thus be approximated by

\[|\phi⟩ = \sqrt{1/2} \left( \alpha_{3/2;1} \phi_{37, 1, 3/2} |1⟩ + \alpha_{1/2;2} \phi_{37, 1, 1/2} |2⟩ \right)\]

(3)

with \(R\)-dependent mixing coefficients \(\alpha_{3/2;1}\) and \(\alpha_{1/2;2}\). For the lower \(^1\Sigma^+\) state correlated to the \(|37, 1, 3/2⟩ |1⟩\) asymptote (dark red curve in Fig. 2a), the absolute square of the coefficient \(\alpha_{1/2;2}\) reaches up to 20% (see inset of Fig. 2), indicating that the hyperfine state of the ground-state atom and the spin-orbit state of the Rydberg atom are strongly entangled. The oscillatory behaviour of the coefficient is a tell-tale sign that the entanglement is a result of the Fermi-Contact interaction. We focus on the \(v = 0\) level of this entangled state, which we refer to as \(\psi_e\) in the following.

The entanglement is observed in PA spectra recorded close to the \(|37, 1, 3/2⟩ |1⟩\) asymptote, depicted in Fig. 2b. Samples of ultracold \(^{39}\)K ground-state atoms released from a magneto-optical trap (\(T \approx 20\) µK, \(\rho = 2 \times 10^{16}\) cm\(^{-3}\)) are prepared in a single hyperfine state. Subsequently, \(^{39}\)K LRM are formed by one-photon photoassociation using UV-laser pulses of 30 µs length and detected state-selectively on an ion detector by pulsed-field ionization \[13\]. To probe transitions to the same molecular states when preparing the ground-state atoms in the \(F = 2\) (II) ground-state hyperfine state, as opposed to \(F = 1\) (I), the laser frequency has to be reduced by twice the ground-state hyperfine splitting (Fig. 1).
both spectra, a strong resonance is observed at a detuning of $-12\text{MHz}$ ($-935.4\text{MHz}$), which is assigned to PA of molecules in state $\Psi_e$. The fact that this resonance is present in both spectra is a clear sign of the mixed $F$ character of this electronic state. From the PA rates normalized to the PA laser intensity and the experimentally determined oscillator strength ratio $f_{j=3/2}/f_{j=1/2} = 3.3(5)$ of the atomic $n^2P_s \leftrightarrow 4^2S_{1/2}$ transition, the admixture of $|37, 1, 2⟩$ is found to be $|α_{1/2}^{3S}/α_{1/2}^{3P}| = 0.17(1)$, which agrees well with the calculated expectation value of $|α_{1/2}^{3S}/α_{1/2}^{3P}| = 0.168$ for $v = 0$ (see Appendix A2). Additional resonances are assigned to levels in the $^3Σ^+$ states correlated to the $|37, 1, 3/2⟩$ and $|37, 1, 1/2⟩$ asymptotes. Because in $^3Σ^+$ states $F$ is conserved, the former (latter) are only observed when preparing the ground-state atoms in $F = 1$ ($F = 2$).

To further probe the electronic character of molecules photoassociated at the resonance assigned to $\Psi_e$, we drive RF transitions $[18, 20]$ to molecular states close to the $|35, 2, j′⟩$ asymptotes. The spin-orbit splitting of the $35^2D_j$ state (with an inverted fine-structure splitting of $27.2\text{MHz}$) is much smaller than the ground-state hyperfine splitting ($461.7\text{MHz}$) and the four dissociation asymptotes resulting from the combination of $j′ = 3/2, j′ = 5/2, F′ = 1$, and $F′ = 2$ group into two fine-structure doublets (Fig. 1). The electronic states correlated to $|35, 2, j′⟩$ $[F′]$ have an almost pure ground-state hyperfine character, the admixture from the other ground-state hyperfine character being less than 0.1%. The potential energy curves of the states correlated to $|35, 2, j⟩$ $[F]$ asymptotes are depicted in Fig. 3a). The $Σ^+$ states correlated to these asymptotes have mixed $j$ character, creating a spectral window above the $j = 5/2$ asymptote where no bound states exist. This gap in the bound-state spectrum allows us to study undisturbed transitions into the continuum above each asymptote. Fig. 3a reveals that transitions to states in the $Π$ continua create free pairs of atoms with the lowest kinetic energy, i.e. the longest de Broglie wavelength, and thus these transitions feature the largest Franck-Condon overlaps with the initial state $\Psi_e$.

Pulsed RF radiation ($\sim 86\text{GHz}$) is obtained by spectrally separating the output of a RF generator. The power of the RF radiation is adjusted by calibrated attenuators after the higher-harmonic generation. To detect RF transitions, we apply a state-selective field-ionization pulse and determine the ratio of ions detected in the time-of-flight-window corresponding to the selective ionization of $35^2D_j$ over the total ion yield. The resulting spectra of the transition from $\Psi_e$ to the $|35, 2, j′⟩$ asymptotes are shown in Fig. 3a), where panel III (IV) depicts the transfer to the $|35, 2, j′⟩$ $[1]$ ($|35, 2, j′⟩$ $[2]$) asymptote. The spectra exhibit strong resonances at the atomic thresholds with a broad shoulder on the high-frequency side, which we attribute to photodissociation into the respective $Π$ continua. The $|35, 2, 1/2⟩$ $[2]$ asymptote forms an exception where no population transfer is observed. This can be understood in the two-state picture of Eq. 3. In $\Psi_e$, the $F = 2$ character is correlated with $j = 1/2$ so that the electric-dipole selection rule...
We simulate the RF spectrum by calculating transition dipole moments, averaged over all accessible electronic states, and assuming an incoherent, irreversible population transfer due to fast dephasing of the continuum wavepackets. The result, depicted in Fig. 3b, reproduces the experimental features attributed to photodissociation transitions almost quantitatively, and features assigned to bound-bound transitions qualitatively. The modeling of bound-bound transitions depends strongly on the details of the computational method [18], and we thus focus on photodissociation rates, which we find to be less dependent on the chosen model. The calculations reveal that the photodissociation occurs almost exclusively into the continuum of $I$ states, resulting in non-interacting photofragments. The sequence of PA of atoms in hyperfine state $F = 1$ into an entangled molecular state and consecutive photodissociation at the threshold of an asymptote with the ground-state atom in hyperfine state $F' = 2$ constitutes a remote quasi-spin flip of the ground-state atom, mediated and heralded through a Rydberg excitation. By additionally harvesting the strong, long-range interaction between Rydberg atoms, this approach could create long-range multiparticle entanglement of ground-state atoms [32, 33].

A closer inspection of the calculated photodissociation rates reveals for some transitions a strong dependence on $\Omega$ of the initial state $\Psi_e$ (Table I). Because of negligible spin-orbit coupling in the electron-K scattering, molecular states of different $\Omega$ are degenerate [18, 34] and not resolved in PA. We employ photodissociation to determine the distribution of $\Omega$ in the photoassociated molecular sample by comparing measured and calculated photodissociation rates. The rates are measured at the respective dissociation thresholds by varying the RF power using a calibrated RF attenuator and fitting a kinetic model of an irreversible reaction of first order to the data (see Appendix A5). For comparison with theory, ratios of photodissociation rates are given in Table I, canceling the unknown absolute intensity of the RF radiation. Numerical simulations show that for comparable initial populations and transfer rates of the $\Omega$ states, the experimentally extracted rate is close to the weighted mean of the transfer rates. We thus determine the relative initial populations in $\Omega = 1/2$ and $3/2$ by minimizing the deviation between the experimental ratios and a weighted mean of the theoretical ratios from Table I, yielding a fraction of 68(6) % of initial molecules in the $\Omega = 3/2$ state. The dependence of the photodissociation rate on the excess kinetic energy $E_k$, controlled by the RF detuning from threshold, yields additional information on the vibrational wavefunction of the initial state $\Psi_e$: as the de Broglie wavelength of the continuum wavefunction becomes shorter than the extent of the initial near-Gaussian wavefunction (Fig. 2), their mutual overlap averages to zero. For an initial Gaussian wavefunction of width $\sigma$ and an interaction-free continuum, the dissociation rates fall off as $\exp\left(-E_k\sigma^2 \right)/\sqrt{E_k}$ [35] (see Appendix A5). With this simple model, we extract $\sigma = 170(80) a_0$ for the initial vibrational wavefunction of $\Psi_e$, which agrees with the value of $99 a_0$ extracted from a fit of a Gaussian to the calculated vibrational wavefunction (see Appendix A5).

We demonstrated the use of photodissociation spectroscopy of LRMs for the characterization of their properties by projection onto an unperturbed atomic basis and comparison to theoretical calculations. We presented a scheme for a complete and remote flip of the hyperfine state of free ground-state atoms through the interaction with a Rydberg atom, where we have exploited the fortuitous near-degeneracy of fine- and hyperfine structure in $^{39}$K $37^2P_j$ states. Similar degeneracies exist in other systems, e.g. in $^{87}$Rb $26^2P_j$ and heteronuclear LRMs ($^{39}$K$^{133}$Cs, Cs$^{53}D_j$) [18, 39]. In the future, the vibrational wavefunction of a LRM might be characterized more precisely by photodissociation to a repulsive PEC [37, 39]. Photodissociation of oriented LRMs [24, 40] might be used to create counter-propagating beams of atoms with well-controlled kinetic energy and entangled internal quantum states.

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### APPENDIX

#### A1. CALCULATION OF POTENTIAL ENERGY CURVES AND TRANSITION DIPOLE MOMENTS

As in previous work [18, 41], we follow Refs. [28, 36] to calculate potential energy curves of long-range Rydberg molecules (LRMs). We adapt the phase shifts from...
Ref. 36, set the semi-classical reference to the next-higher degenerate high-\( l \) manifold, and choose the computational basis to include the Rydberg state of interest, all Rydberg states of the four closest hydrogenic manifolds (two above and two below the target state) and all low-\( l \) Rydberg states within the energy range spanned by the manifolds as well as all hyperfine states \(| F, m_F \rangle \) of the ground state atom. This approach includes partial waves up to \( L = 1 \) in the electron-perturber scattering and we thus include only basis states with \( m_j \leq 3/2 \). The projection of the total angular momentum onto the internuclear axis, given by

\[
\Omega = m_l + m_{s_{\text{Ryd}}} + m_{\text{gs}} + m_i = m_j + m_F, \quad (4)
\]

is a conserved quantity. Here the internuclear axis was set along the laboratory \( z \) axis without loss of generality. However, the value of \( \Omega \) is only of limited use for characterizing electronic states of LRMs, because in general several molecular states of different \( \Omega \) are degenerate. This degeneracy is only lifted by spin-orbit coupling in the electron-perturber scattering [18,34]. We thus find it convenient to label the electronic states of long-range Rydberg molecules not only by \( \Omega \), but also by their dominant character of \( m_l \) (corresponding to \( \Delta \) in the conventional spectroscopic notation), which \( \Sigma \) stands for \( m_l = 0 \) and \( \Pi \) for \( |m_l| = 1 \). We calculate transition dipole moments between electronic states by evaluating the expectation value of the dipole operators \( \mu_0 \) and \( \mu_\pm \) for parallel \( (\Delta m_l = \Delta \Omega = 0) \) and perpendicular \( (\Delta m_l = \Delta \Omega = \pm 1) \) transitions in the molecular frame, where angular matrix elements are evaluated analytically [42] and radial matrix elements are calculated using Numerov’s algorithm and model potentials [43].

Several sets of \( \Sigma \) states exist with binding energies depending only on triplet scattering [19]. We label these states \( ^3\Sigma^+ \) (the superscript “+” indicates the molecular reflection symmetry with respect to a plane containing the nuclei), whereas states with binding energies dependent on both triplet and singlet scattering are labeled \( ^1\Sigma^+ \). These term symbols are however only approximate [24], because the spin-orbit interaction of the Rydberg electron mixes \( m_l = 0 \) and \( |m_l| = 1 \). Thus all \( \Sigma \) states correlated to asymptotes with \( l > 0 \) also have contributions from \( |m_l| = 1 \). This contribution in principle allows for one-photon transitions from the states labeled \( \Sigma \) here to \( \Delta \) \(|m_l| = 2 \) states. Recent theoretical work to also include higher partial waves in the theoretical modeling of LRMs [44] will allow for the inclusion of \( \Delta \) states in future calculations.

### A2. Calculation of Photoassociation Intensities and Mixing Coefficients

To calculate the relative strength of the photoassociation resonances (represented by the height of the bars in Fig. 2b) of the main article we assume that there is no fixed phase relation of the colliding ground-state atoms over the range of the vibrational wavefunction of the photoassociated LRM. This assumption is reasonable, because the thermal de Broglie wavelength of \( ^{39}\text{K} \) atoms at 20 \( \mu \)K is about 1000 \( a_0 \), much shorter than the inter-nuclear separations considered here, and several partial waves contribute to the initial scattering wavefunction at the equilibrium distance of the photoassociated molecules \( R_c \sim 2350 a_0 \). For a homogeneous gas of atoms initially prepared in the hyperfine state \( F \), the relative photoassociation rates were consequently estimated through the expression

\[
\Gamma^{F}_{\kappa,\nu} = \gamma^{PA}_{\kappa} \sum_{j} f_j \int R^2 |\Psi_{\kappa,\nu}(R)|^2 |\alpha^e_{j,F}(R)|^2 dR, \quad (5)
\]

where \( \kappa \) labels the electronic state addressed in PA and \( \Psi_{\kappa,\nu} \) is the vibrational wavefunction of level \( \nu \) (see Supplementary Material of Ref. [18]). The global coefficients \( \gamma^{PA}_{\kappa} \) contain e.g. electronic transition dipole moments and PA intensities and were determined by comparison with the experimental spectra, while the ratio of the atomic \( ^3P_2 \) \( P_j \leftarrow 4^2S_{1/2} \) transition dipole moments was determined experimentally to be \( F = f_j = 3/2 / f_j = 1/2 = 3.3(5) \). The deviation from the statistically expected ratio of 2:1 results from a Cooper minimum in the photoionization cross section [35]. The absolute squares of the mixing coefficients \( |\alpha_{j,F}^e| \) are obtained by the expression

\[
|\alpha_{j,F}^e(R)|^2 = \sum_{m_j, m_F} |\langle 37, 1, j, m_j, F, m_F | \phi_e(R) \rangle|^2, \quad (6)
\]

where \( \phi_e(R) \) is the electronic wavefunction of the photoassociated state.

Experimentally we observe a ratio \( R = 3.5(1) \) of \( \Psi_e \) PA rates when preparing atoms initially either in \( F = 1 \) or \( F = 2 \). After normalization to the ratio of PA UV powers \( P = 4.7(1) \) and the ratio of oscillator strengths \( F \), the absolute squares of the mixing coefficients \( |\alpha_{3/2,1}^e|^2 \) and \( |\alpha_{1/2,2}^e|^2 \) can be extracted by

\[
\frac{|\alpha_{3/2,1}^e|^2}{|\alpha_{1/2,2}^e|^2} \approx 1 - \frac{|\alpha_{1/2,2}^e|^2}{|\alpha_{1/2,2}^e|^2} = \frac{RP}{F}, \quad (7)
\]

where all other mixing coefficients were assumed to be zero. The resulting mixing coefficient of the state \( \Psi_e \) is

\[
|\alpha_{1/2,2}^e|^2_{\text{exp}} = 0.17(1), \quad (8)
\]

which is in good agreement with the expectation value of \( |\alpha_{1/2,2}^e|^2_{\text{theo}} = 0.168 \) for state \( \Psi_e \), calculated from the vibrational wavefunction and \( R \)-dependent mixing coefficient depicted in Fig. 2a) of the main article.
A3. CHARACTERIZATION OF A STATE WITH PURE F CHARACTER

For completeness, we also present a photodissociation spectrum of molecules photoassociated in the \( v = 0 \) level of the \( ^3\Sigma^+ \) state below the \( |37, 1, 3/2\rangle |1\) asymptote. The resulting RF spectra close to the \(|35, 2, j'\rangle |1\) (III) and \(|35, 2, j'\rangle |2\) (IV) asymptotes are depicted in Fig. AI. The RF spectrum in the vicinity of the \(|35, 2, j'\rangle |1\) asymptotes is qualitatively very similar to the RF spectrum obtained for the entangled \( \Psi_\text{e} \) state, containing features assigned to bound-bound and bound-continuum transitions. The RF spectrum in the vicinity of the \(|35, 2, j'\rangle |2\) asymptotes, however, does not show any population transfer, confirming the pure \(|37, 1, 3/2\rangle |1\) character of the unentangled molecular \(^3\Sigma^+\) state.

A4. SIMULATION OF RADIOFREQUENCY PHOTODISSOCIATION SPECTRA

To simulate the RF spectra, we treat regions containing bound molecular states (shaded in gray in Fig. 3 b) of the main article) and regions containing transitions into the photodissociation continua separately. We thus neglect the multi-channel nature of the problem, which is a good approximation due to the relatively large separation of the respective spectral regions. Franck-Condon factors for transitions to all electronic states are determined from the calculated \( R \)-dependent transition dipole moments and wavefunctions of the nuclear motion obtained from a modified Milne phase-amplitude method [18, 46]. Bound-continuum transitions are energy normalized with respect to the corresponding molecular asymptote. We define the phase of vibrational wavefunctions in the bound region by setting it to zero in the classically forbidden region at large internuclear separations. In contrast, the phase of the continuum wavefunctions is only restricted through boundary conditions at short internuclear distances, where the approximations of our theoretical model break down. Additionally, several partial waves (corresponding to the molecular rotation \( N \) in “conventional” molecules) contribute at a given dissociation energy. We thus assume a uniform distribution of scattering phases and average the transition rates incoherently over all phases. The transition rates are calculated in the molecular frame. We neglect the rotational HönL-London factors because the rotational states are experimentally not resolved.

The resulting stick spectra are convoluted with a Lorentzian line profile of 200 kHz FWHM (transform limit of the 5 \( \mu \)s RF pulse), resulting in a simulated spectrum \( \gamma(\nu) \) with the relative transition strengths on resonance listed in the column “vibronic” of Table AI. In this table, we compare the results of this simulation to two simpler models. In the “atomic” approximation, only the relative transition strengths of the basis states in the two-state approximation (Eq. (3) of the main article) are evaluated via the Wiguna-Eckart theorem [42] and the mean value of the mixing coefficient \( |\alpha|_1^2 + |\alpha|_2^2 \) is \( 0.18 \), which does not depend on \( \Omega \). To refine this estimate, we calculate the expectation values of the dipole moments for transitions to \( \Pi \) states with respect to the initial vibrational level \( \Psi_\text{e} \). The resulting rates capture the rel-
RF source was kept fixed at the respective dissociation thresholds. The frequency of the mental and theoretical photodissociation rates, we also found contribution to the different normalization conditions for the final bound and continuum wavefunctions. The results, shown as full lines in Fig. 3 b) of the main article, we account for the observed transitions, but deviate still significantly from the experimental values. The “vibronic” calculation predicts overall smaller ratios, which we attribute to the averaging of the diverging photodissociation rates at threshold and, to a lesser extent, to the inclusion of transitions into the continuum of Σ states.

For comparison with the experimental spectrum in Fig. 3 b) of the main article, we account for the observed saturation of the RF transfer by applying an empirical saturation function of the form $A [1 - \exp (-\gamma(\nu)/I_{\text{sat}})]$ to the calculated spectrum $\gamma(\nu)$ and extract the two parameters $A$ and $I_{\text{sat}}$ in a global least-squares analysis. The results, shown as full lines in Fig. 3 b) of the main article, agree well with the experimental data. We found it necessary to scale bound-bound and bound-free spectra with two different sets of parameters, which we attribute to the different normalization conditions for the final bound and continuum wavefunctions.

A5. EXPERIMENTAL DETERMINATION OF THRESHOLD PHOTODISSOCIATION RATES

For a more quantitative comparison between experimental and theoretical photodissociation rates, we also determined experimental photodissociation rates at the respective dissociation thresholds. The frequency of the RF source was kept fixed at the respective dissociation maxima (compare Fig. 3 b) of the main article), and its power was varied using a calibrated RF attenuator. We then record the fraction $Q$ of ions detected in the time-of-flight windows set for $37^2P \rightarrow 35\Sigma$ transitions. The rates at 0 MHz RF detuning (gray data points) were not included into the fit because of the divergence of the theoretical model at this point.

Figure AIII. Energy-dependence of photodissociation rates from the $\Psi_1$ state to the $|35, 2, 3/2 \rangle \{1\}$ (green), $|35, 2, 5/2 \rangle \{1\}$ (blue), and $|35, 2, 3/2 \rangle \{2\}$ (brown) asymptotes obtained from fits to power-dependent measurements at different RF detunings above the dissociation threshold. The error bars indicate the standard deviation of the fitted rates. The simple model explained in the text predicts the energy dependence $\gamma(E_k)$ given on the figure. Here, $A_{F,F}$ is an arbitrary, asymptote-dependent amplitude, $\mu$ the reduced mass of the molecule in atomic mass units, $E_D$ the detuning from threshold in megahertz, and $\sigma$ the Gaussian width of the initial molecular state in Bohr radii. The red curve is a global fit of this model to the data points, weighted by their standard deviations, with free parameters $A_{3/2,1}$, $A_{3/2,2}$, $A_{5/2,1}$, and $\sigma$. The shown photodissociation rates are normalized by the fitted amplitudes $A_{F,F}$. The rates at 0 MHz RF detuning (gray data points) were not included into the fit because of the divergence of the theoretical model at this point.
in a global fit of the amplitude $A$ of the transition, rate of transfer $k_\kappa$ ($\kappa = \{ j, F \}$), and signal offsets $O_P$ and $O_D$, to the experimental data presented in [Fig. AII]. The resulting fit parameters are reported with their statistical uncertainties on the figure and the obtained ratios of transition rates are reported in Table I of the main article.

Finally, we study the energy-dependence of the photodissociation rates above threshold in more detail. To this end, we repeat the measurement and analysis outlined above at several energies above threshold. The results are shown in Fig. AIII normalized to the global fit of the model function shown on the figure. The model function is obtained by analytically solving the overlap integral of a Gaussian wave function with width $\sigma$ and a $s$-wave continuum wavefunction of the form

$$1/\sqrt{k} \sin(kR),$$

where $k$ is the magnitude of the continuum wavevector and $R$ the interatomic separation, and extracting the envelope of the resulting oscillating function [35]. At fit of this model to the experimental rates reproduces the experimental observations and yields a value $\sigma = 170(80) \, a_0$ where the reported uncertainty is the statistical uncertainty of the nonlinear regression.

\[ Q_{37P, \kappa} = A \exp[-k_\kappa I_{rel}] + O_P \]  
\[ Q_{35D, \kappa} = A (1 - \exp[-k_\kappa I_{rel}]) + O_D \]  

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