Rotationally Resolved Fano Effect of HI Molecules: An Experimental Study Using Coherent Vacuum-Ultraviolet Radiation

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An experiment studying the influence of molecular rotation in Hi on photoelectron-spin polarization is presented. The experiment is highly wavelength selective since a laser-based vacuum-ultraviolet-radiation source with a bandwidth of 0.5×10^{-4} nm is applied to produce circularly polarized light. Although in the Fano effect the kinetic energy of the photoelectrons is not analyzed, rotational structure is resolved via narrow-band excitation of autoionization resonances. The photoelectron-spin polarization is found to be strongly affected by the rotational substructure, leading to changes in both magnitude and sign for different rotational lines.

A quantum mechanically "complete" characterization of the atomic photoionization process[1] can be obtained by studying the photoelectron-spin polarization in addition to the partial cross sections and photoelectron angular distributions. Electron-spin-resolved measurements in atomic photoionization using circularly polarized radiation have yielded highly specific data (isolated matrix elements and phase-shift differences) on the photoionization dynamics.[2] According to Fano's prediction,[3] atomic photoelectrons may be highly spin polarized even if they are extracted by an electric field, regardless of their direction of emission (Fano effect[1]).

For free molecules, the photoionization process is more complicated as a result of their lower symmetry and the presence of molecular vibration and rotation. In past investigations of the photoelectron-spin polarization, only the electronic structure including spin-orbit fine structure was taken into account theoretically[4,5] and resolved in experiments,[6] which predominantly used circularly polarized synchrotron radiation. Until now, the influence of molecular rotation on the photoelectron-spin polarization has been neither examined experimentally, because of the limited resolution of radiation monochromators and electrons spectrometers, nor calculated theoretically. Although a general theoretical treatment of the influence of molecular rotation on photoelectron emission began very recently,[7] up to now no numerical prediction exists for the effects of molecular rotation on the spin polarization of photoelectrons. In recent years narrow-band coherent vacuum-ultraviolet (VUV) light sources have become available[8] which have much higher resolving power, at comparable radiation intensities, than monochromators using synchrotron radiation. With such a laser-based source molecular rotation can be resolved in the photoionization via autoionizing states, and the influence of rotation on the photoelectron-spin polarization can be examined even if the kinetic energy of the photoelectrons is not analyzed. In this Letter we report on rotationally resolved measurements of the electron-spin polarization in the spin-orbit autoionization region

of hydrogen iodide in an emission-angle–integrated experiment (Fano effect[1]). HI was chosen because of its large spin-orbit splitting, because of the presence of pronounced autoionization resonance structures,[9] and because a theoretical prediction[5] (which did not include rotation) was available.

Remarkable progress was made in the past decade in spin-unresolved molecular multiphotoionization, enabling rotationally resolved studies.[10] In the present work we favor single-photon ionization using pulsed dye-laser radiation, which is frequency upconverted to the VUV. For the conversion we choose resonantly enhanced sum-frequency mixing in mercury vapor.[8] When operated at a wavelength of around 116 nm ($86\,207$ cm^{-1}), this source delivers $\approx 10^{11}$ photons/sec into the target at a bandwidth of 5×10^{-4} nm (0.37 cm^{-1}). This radiation is used to ionize a supersonic beam of HI molecules that is rotationally cool, with only two ground-state rotational levels populated considerably at ≈ 13 K. Regardless of their direction of emission, all photoelectrons produced are extracted by an electrostatic quadrupole field[11] and accelerated to 100 keV for an analysis of their intensity and their spin polarization in a Mott detector.[11]

Our experimental setup, shown in Fig. 1, uses two Nd-doped yttrium-aluminum-garnet–pumped dye lasers (11-Hz repetition rate). The frequency of one laser is doubled by use of potassium dihydrogen phosphate crystal and tuned to match the Hg $6s\,^1D_2$ resonance. The other laser can be tuned throughout the visible part of the spectrum. Both beams are spatially overlapped by a dichroic mirror and focused ($f = 100$ cm) into the mercury cell. The homogeneous zone of mercury vapor ($p = 10$ mbar), used as conversion medium, is prepared in a heat-pipe construction[8] buffered with 13 mbar of neon. A LiF prism separates the sum-frequency from the intense input beams and unwanted by-products of the conversion,[8] and a MgF$_2$ quarter-wave plate changes the polarization of the VUV from linear to circular. After passing the target region, the intensity of the beam is monitored with an open photodiode; alternatively, the
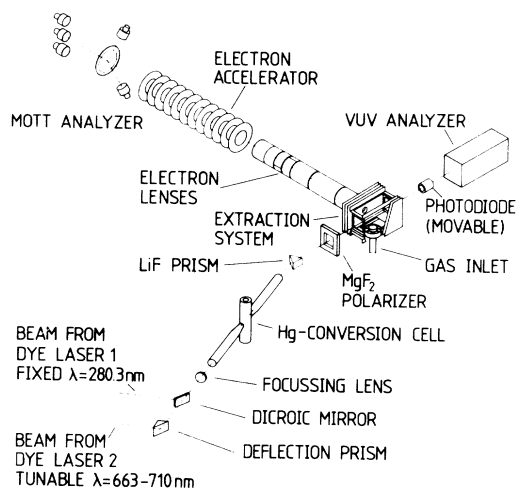
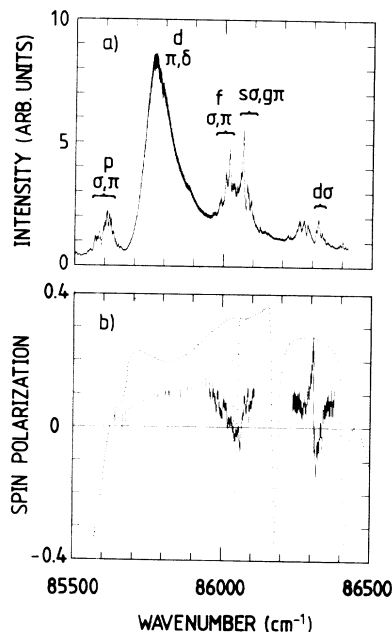FIG. 1. Schematic view of the experimental setup.

FIG. 2. Measured photoelectron yield from a jet-cooled HI sample (upper part) and the corresponding electron-spin polarization (lower part). All experimental data are plotted as vertical error bars, indicating their experimental uncertainties. Additionally, the result of an *ab initio* calculation (Ref. 5) is shown as a dotted line in the lower part.

polarization can be checked by an analyzer (reflection type, using four gold mirrors). Typically, 10^{10} photons per pulse, with a degree of circular polarization of more than 96%, are detected.

The autoionization region of HI (autoionizing Rydberg states converging to the $^2\Pi_{1/2}$ $v = 0$ ionic state which couple via spin-orbit interaction to the continua of the $^2\Pi_{3/2}$ $v = 0$ ionic state) shows pronounced resonance structures,[9] connected with HI Rydberg states $(5p\pi)^3 nl\lambda$. Although states in the Rydberg order $n_{\text{eff}} = 5$ have sufficient energy to autoionize, we examined the order $n_{\text{eff}} = 6$, since an *ab initio* calculation of the dynamical parameters exists[5] for this energy range $(85\,500-86\,500$ cm$^{-1})$. In the upper part of Fig. 2 the total photoelectron yield is shown for this complete Rydberg order. The spectrum is dominated by a broad resonance which can be assigned to $d\pi$ and $d\delta$ states.[5,12] Sharp resonances due to $f\sigma,\pi$, $s\sigma$, $g\pi$, and $d\sigma$ states can be detected superimposed on the wing of the main d structure. It is worth noting that because of rotational structure the number of resonances observed greatly exceeds the number of electronic states assigned. For molecules, the orbital angular momentum of the electron is not a good quantum number, and l mixing, i.e., coupling between states of the same λ and different l, has to be considered using this classification.[5] Evidence for a perturbation is given by the irregular rotational spacings between the three different lines of the $d\sigma$ resonance, where one of them (the Q_1 line) is barely detectable as a shoulder in the strong R_0 peak at $86\,320$ cm^{-1}.

In the lower part of Fig. 2 the spin polarization measured is plotted together with the results of the *ab initio* calculation of Ref. 5. The experimental data, plotted as vertical error bars denoting the experimental uncertainties, exhibit, in general, positive values of about $+10\%$. Corresponding to the sharp features in the yield spectrum, many sharp resonances appear in the spin-

polarization data. The results of the *ab initio* calculation,[5] which neglects any rotational or vibrational effects, are shown as a dotted curve; they disagree with the experimental data in the absolute degree of the polarization and the position of the resonances, which is not surprising in view of the effects neglected. They agree, however, in the occurrence of an overall positive background polarization and negative polarization values in the sharp resonances.

The most prominent structure of the experimental spin-polarization data is a resonance at $86\,315$ cm^{-1}. It can be assigned to the perturbed $d\sigma$ complex; hence an easy rotational analysis is hampered. For this reason we focused our further attention on the resonances between $86\,000$ and $86\,100$ cm^{-1}. This spectral region is shown in more detail in Fig. 3 on an enlarged scale. Curve a is a magnification of the central part of Fig. 2(a), whereas curve c shows in detail the corresponding spin polarization of Fig. 2(b). Both spectra exhibit many overlapping resonance structures. The bandwidth of the VUV radiation is at least 3 times smaller than the spacing between two data points in the plots shown and it is smaller than the autoionization linewidths. The largest obstacle for an analysis of the spin-polarization data with respect to the influence of rotational effects is an overlap between rotational branches of different electronic states.

In order to solve this problem, a simple simulation of the yield curve was performed (curve b), based upon
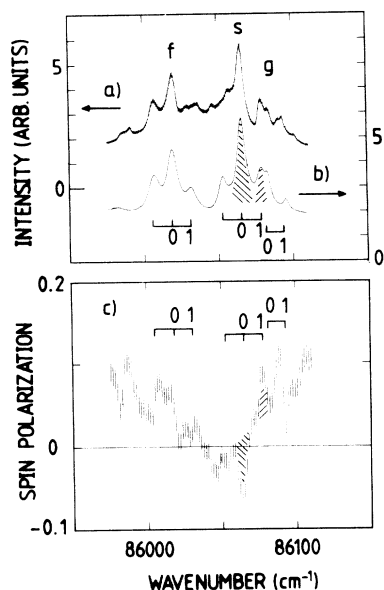
FIG. 3. Curves a and c show an expanded view of the central part of Fig. 2, the measured yield curve and the corresponding electron-spin polarization. Curve b is the result of a fit explained in the text. In curves b and c the sequence of the Q, R_0, and R_1 lines (from left to right) belonging to the $s\sigma$ and $f\sigma$ states, as well as the R_0 and R_1 lines of $g\pi$, are indicated.

TABLE I. Parameters of the fit corresponding to curve b, Fig. 3. Temperature, 13.0 K.

a	l,λ	μ_a	q_a	σ_a	B_0'
1	$s\sigma$	0.0310	9.5	0.160	6.6
2	$p\sigma$	0.4600	11.0	0.040	6.3
3	$d\sigma$	−0.2340	8.5	0.080	6.4
4	$f\sigma$	0.0750	9.0	0.105	6.4
5	$p\pi$	0.4320	5.5	0.100	6.3
6	$d\pi$	0.3010	4.5	0.300	6.3
7	$f\pi$	0.0850	8.0	0.020	6.1
8	$g\pi$	0.0120	12.5	0.010	6.2
9	$d\delta$	0.3150	2.8	0.500	6.3

several crude approximations. The Rydberg states were treated independently, assuming interaction with one continuum only; furthermore, the validity of the Born-Oppenheimer approximation was assumed. Starting from the quantum defects μ_a of the nine Rydberg series $(a=1-9)$ predicted by the calculation,[5] first the positions of all lines were determined using the Rydberg formula and the J-dependent spacings[13] between rotational lines for Hund's case c. The corresponding transition probabilities were calculated by multiplying a transition moment σ_a, characteristic for all members of a series, with the thermal distribution of J levels in the ground state and the Hönl-London factors.[13] Using Fano's formulas[14] for the interaction of a single autoionization resonance with a single continuum, a profile of each line was generated. In a last step the contributions from all rotational lines were added up incoherently to produce the final spectrum (curve b in Fig. 3), which is compared to the experimental data (curve a). The following slightly adjustable input parameters were used in the simulation: The temperature of the sample, the rotational constant of the excited state $B_0'(a)$, the quantum defect μ_a, the transition moment σ_a, and the line-shape factor q_a. Curve b shows the best fit obtained applying the procedure described above, and the parameters finally used are listed in Table I.

The most intense peaks were reproduced quite well. However, deviations indicating the limitations of the approximations made are observed in three structures of

the spectrum: the central part between the f and s peaks, where the measured intensity varies only slightly, and the structures connected with the sharpest resonances in the spin-polarization data at 85985.8 and 86094.8 cm^{-1}. Since at 13 K the R_0 lines should be the most intense resonances, an unambiguous assignment could be made only for the two R lines of the $s\sigma$ state (see the shaded areas of curve c). Because of severe overlapping, similar results for different classifications were obtained in the region of the f complex $f\sigma,\pi$. Our assignments of the Q, R_0, and R_1 lines belonging to the $s\sigma$ and $f\sigma$ states, as well as the $g\pi$ R_0 and R_1 lines, are indicated in Fig. 3, curves b and c.

The spin polarization (curve c) exhibits structure with energy intervals between the different peaks which are equal to the rotational spacings. Most of these peaks are strongly correlated with resonances in the yield curve. Compared to the spin-polarization values in their direct neighborhood, some of these polarization peaks show an upwards trend while others go downwards. These observed changes of sign in the resonant contributions must be due to rotational effects, since the separation between the resonances is the rotational spacing as denoted in Fig. 3, curve c. In particular, the data show that the two lines R_0 and R_1 of the same electronic Rydberg state $(s\sigma)$ have spin-polarization values of opposite sign.

In order to get more quantitative insight, a theoretical calculation of spin-resolved molecular photoionization taking into account rotational effects is needed. As we know, this is in progress.[15]

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