Evidence for a Molecule-Rotation-Dependent Spin Polarization Transfer Mechanism in the Photon-Induced Autoionization of HCl and DCl

M. Drescher, R. Irrgang, A. Elizarov,* N. Böwering, and U. Heinzmann
Universität Bielefeld, Fakultät für Physik, 33501 Bielefeld, Germany

(Received 31 October 1994; revised manuscript received 24 July 1995)

High resolution spectra of the angle-integrated photoelectron spin polarization, after excitation of HCl and DCl with circularly polarized laser radiation, reveal pronounced rotational autoionization structures. The data, interpreted in terms of Rydberg series converging to limits with different ionic angular momenta of the $^2\Pi_{1/2}$ fine structure component, clearly indicate a systematic dependence of the sign of the spin polarization on the rotation of the molecular ion core. Application of the current theoretical model leads to consequences for the angular momentum transfer in the autoionization process.

PACS numbers: 33.80.Eh

The process of photoionization using circularly polarized radiation can be looked upon as a transfer of energy and angular momentum from photon to photoelectron. For the case of free atoms the spin polarization transfer, due to the existence of the spin-orbit interaction, has been investigated for many systems [1]. Our interest is now directed to molecules, where the question arises to what degree the spin polarization transfer process is influenced by the specific angular momentum of the rotation of the molecular ion core. Very recently, an experimental study [2] on nitric oxide demonstrated a clear alternation of the sign of the angular distribution asymmetry parameter β for consecutive rotational levels. In a previous experimental study [3] of the angle-integrated spin polarization of photoelectrons from HI after excitation with circularly polarized light (Fano effect [4]), indications for a variation of the magnitude of the spin polarization for different rotational lines were found. However, this observation was limited to a single Rydberg order, where the correct assignment of rotational lines is not unambiguous and is still under discussion [5,6]. In order to find a systematic dependence of the spin polarization value or even its sign on molecular rotation, it is necessary to choose a target where the rotational progression can be investigated for several Rydberg orders and where a clear assignment of the observed features in the spin polarization to distinct rotational levels is possible. These conditions were found to be fulfilled for the halides HCl and DCl. We studied the Fano effect in the energy region between the $^2\Pi$ fine structure components, where Rydberg series converging to rotational limits of different total angular momentum J_c of the $^2\Pi_{1/2}$ molecular core lead to autoionization resonances [7,8]. According to a multichannel quantum defect treatment [9], the angular momentum coupling case in the investigated region is close to Hund's case (*e*), which means that the angular momentum of the Rydberg electron is fully decoupled from molecular axis. In spite of the relatively large rotational constants, 9.8 cm^{-1} for HCl^+ and 5.1 cm^{-1} for DCl^+, the multitude of overlapping progressions leads to very complex spectra. This calls for efficient rotational cooling of the ground state molecules, such that only transitions from the lowest rotational state can occur, and for highly selective excitation with a resolving power greater than 10^5 at photon energies of more than 12.7 eV in order to separate the different rotational levels of the autoionization resonances.

The experimental setup for the rotationally resolved analysis of the total electron spin polarization (see Fig. 1) is an extension of a previously described apparatus used for the measurement of the total ionization yield [7] by excitation, with narrow band radiation generated by resonant sum-frequency mixing of two pulsed laser beams in xenon. A zero-order quarter-wave plate was inserted to convert the linear polarization of the fundamental laser beams to circular polarization. This polarization state is preserved during the mixing process. Since angular momentum conservation requires an intermediate resonant state of the nonlinear medium with a total angular momentum $J = 2$ for the generation of circularly polarized light, we chose the $5p$-$6p'$ $(\frac{3}{2}, 2)$ transition of xenon at $\lambda = 224.3$ nm. Unfortunately, the use of this transition

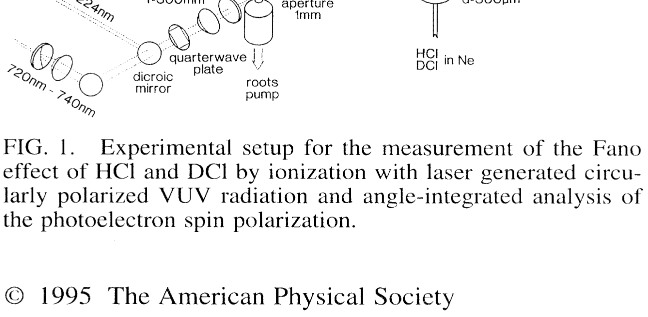

FIG. 1. Experimental setup for the measurement of the Fano effect of HCl and DCl by ionization with laser generated circularly polarized VUV radiation and angle-integrated analysis of the photoelectron spin polarization.

0031-9007/95/75(16)/2936(4)$06.00

results in a reduction of the conversion efficiency by a factor of 10, compared to the very efficient resonant transition $5p$-$6p'$ $(\frac{1}{2},0)$ at $\lambda = 222.6$ nm, which has been used for the generation of up to 10^{10} photon/s, however, only with linear polarization [7]. Using a polarization analyzer consisting of four turnable gold mirrors [10], the degree of circular polarization for both helicities, P_{circ}, was determined to be larger than 0.99. The neon seeded and skimmed molecular beam of HCl and DCl, as well as the cylindrical ionization cage for angle-integrated photoelectron collection, are the same as for the yield measurements [7]. Electron spin polarization analysis was performed using a Mott analyzer, as described in Ref. [3]. The analyzing power of this Mott analyzer, i.e., the effective Sherman function S_{eff}, was determined to be 0.23 ± 0.02 by using xenon atoms as the photoionization target for calibration to the spin polarization parameter of the Xe $7d$ autoionization resonance, which is well known from a previous investigation with synchrotron radiation [11].

The photoionization experiment was performed in the photon energy region between 102 850 and 103 050 cm^{-1}, where a previous study [7] has led to an assignment of the resonances observed in the total ionization yield spectra. For higher wave numbers the spectrum becomes irregular and cannot be interpreted plainly in a Hund's case (*e*) frame. The autoionization resonances converge to the $^2\Pi_{1/2}$ ionization limit and consist of a series with a molecular core of total angular momentum $J_c = 1/2$ or $3/2$. In Figs. 2 and 3 we present the results of the measurement of the angle-integrated spin polarization, the so-called A parameter [1] of HCl and DCl, respectively. Because of the efficient rotational cooling in the supersonic target beam, essentially only transitions from the rotational ground state contribute to the spectra. The comparably large error bars of the spin data reflect the fluctuations of the detector currents, which were more than three orders of magnitude smaller compared to the yield measurements. While the displayed intensity data were obtained with 50 laser shots for each wave number step, the value for each data point for the A parameter is the mean value of at least three independent sessions on different days, with a total of more than 4800 laser shots. In addition to the statistical errors, the vertical scale of A is subject to a relative uncertainty of 8% due to the errors in the determination of S_{eff} and P_{circ}.

Extreme values in A are in most cases correlated with peaks in the intensity, thus enabling a direct assignment of features in A to distinct resonances. The structure at 102 920 cm^{-1} in HCl exceeds an A value of +0.5, which has been shown to be an upper limit for A in a theory [12] describing the photoionization of unoriented molecules in Hund's cases (*a*) and (*b*). However, a more recent theoretical approach [13] confirms that values of $|A|$ larger than 0.5 are in fact possible in the rotationally resolved photoionization of molecules in Hund's case (*e*). For low Rydberg orders, as observed in HI [5], resonances belonging to d series can easily be identified due to their broad and asymmetric profile, resembling the autoionization resonances of the noble gases [14]. For the spin-orbit autoionization of HCl and DCl, such a simple identification based on the intensity spectra is not possible. The spin polarization parameter A as a signed value provides additional spectroscopic information in the form of structures with positive or negative trends. Resonances with different tendencies should belong to series with different physical properties. A systematic scheme can be established by associating the tendency of A with the total angular momentum J_c of the molecular core. If we attribute positive and negative tendencies of A to a quantum number $J_c = 1/2$ and $3/2$, respectively, it is possible to assign the vast majority of observed resonances in HCl, as indicated in Fig. 2. In this spectrum, structures of the same tendency often appear as doublets of lines, indicated by brackets, with a separation compatible with quantum defect differences of s and d series of typically 0.15 [7]. The distance between positive and negative doublets is

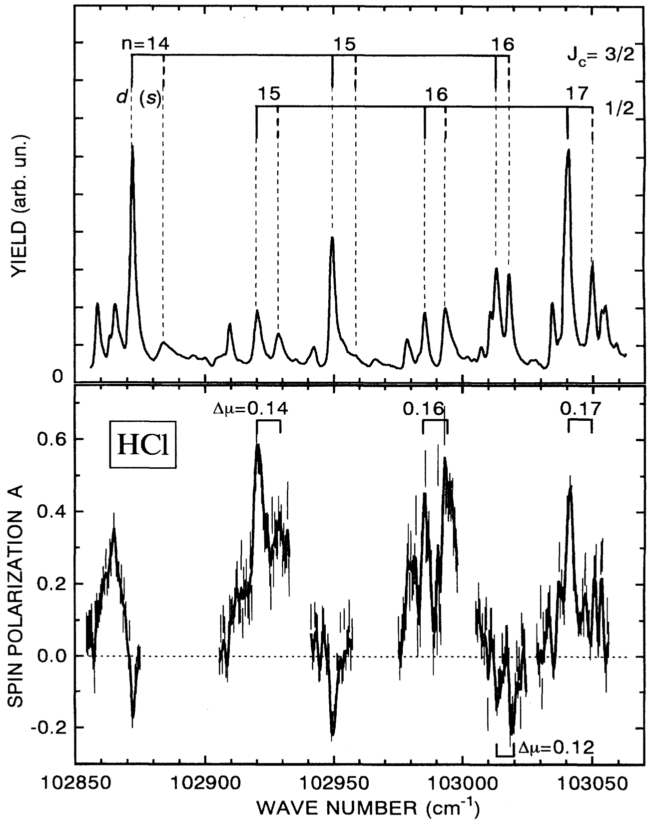

FIG. 2. Results for the total ionization yield (upper frame) and the angle-integrated spin polarization A (lower frame) of photoelectrons from HCl. Vertical bars indicate the statistical error. Full lines represent a convolution of the data with a width of 1 cm^{-1}. The scale of A has an uncertainty of 8%.

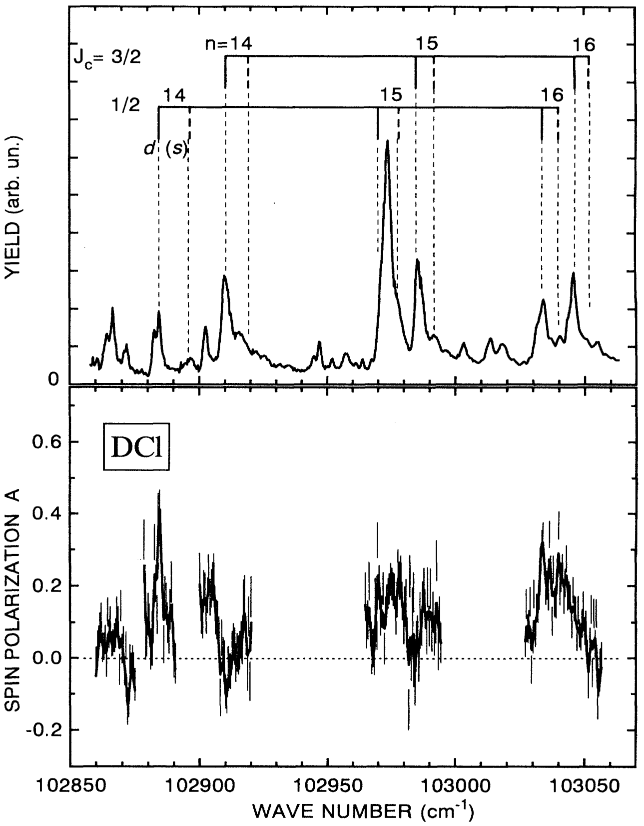

FIG. 3. Results for the total ionization yield (upper frame) and the angle-integrated spin polarization A (lower frame) of photoelectrons from DCl. Vertical bars indicate the statistical error. Full lines represent a convolution of the data with a width of 1 cm^{-1}. The scale of A has an uncertainty of 8%.

found to be approximately 30 cm^{-1}. This is equal to the difference between the $J_c = 1/2$ and 3/2 ionization limits, which were determined experimentally using ZEKE spectroscopy [15,16]. For most of the lines this assignment is consistent within a few cm^{-1} with the previous assignment, based on a quantum defect analysis of the intensity data [7] of HCl and DCl. It is also supported generally by the data for DCl, using an assignment as given in Fig. 3. For DCl the dynamic range of A values is significantly smaller than for HCl, probably due to a partial cancellation of contributions of opposite signs resulting from the reduced separation of the resonances in comparison to HCl, which has a 2 times larger rotational constant. The prominent peak at 102 973 cm^{-1}, which does not fit well into this pattern, may belong to a series converging to a higher electronic or vibrational threshold. However, both an experimental determination [3] as well as a calculation [17] of the parameter A of the heavier hydrogen halide HI have exhibited positive values of A for d resonances and negative values for s resonances. Using that scheme for the interpretation of the HCl and DCl spectra, one would expect to find pairs of d and s resonances with positive and negative tendency in A, respectively, that are separated by some 10 cm^{-1} in the considered range of Rydberg orders. Such patterns can only be found at energies around 102 870 and 102 950 cm^{-1} in HCl or around 102 910 cm^{-1} in DCl, but a corresponding assignment would imply that S resonances are much stronger than d resonances, which is clearly in contrast to the behavior of these series in the rare gases as well as in HI [5]. Moreover, the majority of observed lines remains unassigned if the spectra are analyzed by postulating this pattern.

The interesting point in the assignment given in Figs. 2 and 3 is that the total ionic angular momenta $J_c = 1/2$ and 3/2 differ only in the rotational angular momentum $\vec{N}$ which forms $\vec{J}_c$ together with the projection Ω_c on the molecular axis. We have therefore found evidence for a transfer of spin polarization from the incident circularly polarized photon to the outgoing electron that is dependent in sign and quantity on definite states of molecular rotation. A dependence of the photoelectron spin polarization exclusively on electronic angular momenta would require a completely perturbed behavior of the relative cross sections and the quantum defects of the Rydberg series.

In a recent theoretical description [18] of the molecular ionization, including rotation analytical expressions for the dynamical photoionization, parameters have been derived. The expression for the parameter A for photoelectrons with orbital angular momentum l and total angular momentum j reads

$$A(J^+) = \frac{\sum_{l,j} c_{l,j} d_{l,j}^2 + \sum_{l,j,j'} c_{l,j,j'} \mathrm{Re}(d_{l,j}^* d_{l,j,j'})}{\sum_{l,j} d_{l,j}^2}, \tag{1}$$

where $d_{l,j}$ denotes transition moments, and $c_{l,j}$ and $c_{l,j,j'}$ are signed scalar weighting factors. It should be noted that in this description the A values are given for transitions from the ground state to the continuum of states with specific total angular momentum J^+ of the ion and a projection $\Omega^+ = 3/2$, while in our experiment we observe resonances belonging to bound states with a J_c, $\Omega^+ = 1/2$ molecular core. Applying Eq. (1) to the case of HCl with a $J'' = \Omega'' = 0$ ground state, one finds a negative $c_{2,j}$ only for $J^+ = 3/2$. Thus for d resonances, the experimentally observed dependence of the sign of A on J_c is compatible with this model if one assumes that series converging to the $\Omega_c = 1/2$, $J_c = 1/2$ ($J_c = 3/2$) limit decay preferentially into the $\Omega^+ = 3/2$, $J^+ = 5/2$ ($J^+ = 3/2$) continua (see Fig. 4). Unfortunately, expression (1) does not yield the observed positive sign of s resonances converging to a $J_c = 1/2$ limit, since conservation of the total angular momentum $\vec{J} = \vec{J}_c + \vec{j}$ restricts the allowed J^+ values for $J = 1$ and $l = 0$ (assuming constant $j = 1/2$) to $J^+ = 3/2$ for which $c_{0,1/2}$ is negative. The proposed assignment for s lines is therefore less evident than for d lines.

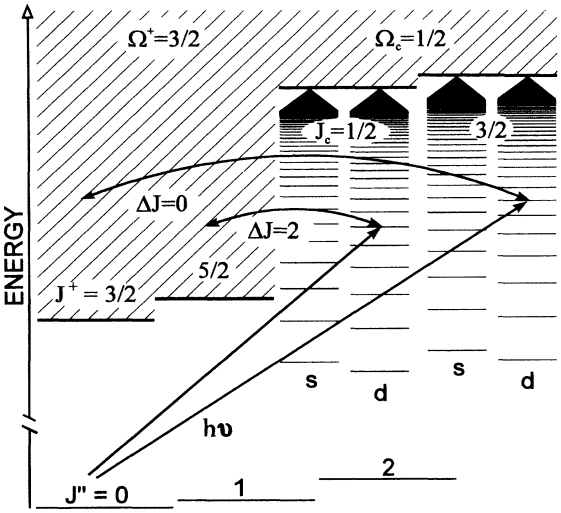

FIG. 4. Diagram of series in HCl and DCl, converging to rotational states J_c of a $^2\Pi_{1/2}$ core and autoionizing into the continuum of a $^2\Pi_{3/2}$ ion with total angular momentum J^+.

Our results stimulate the fundamental question in which manner the total angular momentum of the molecular core changes during the autoionization process. The decay of series converging to the $\Omega_c = 1/2$, $J_c = 1/2$ limit must obviously be accompanied by a change, $\Delta J = J^+ - J_c \geq 1$, since no $\Omega^+ = 3/2$, $J^+ = 1/2$ continuum is available. Moreover, application of the theoretical model to the observed dependence of the total spin polarization on molecular rotation requires a pronounced variation $\Delta J \neq 0$ during autoionization For $\Delta J = 0$, the transition from $\Omega_c = 1/2$ to $\Omega^+ = 3/2$ can be compensated by an equivalent change of the molecular rotation without any angular momentum transfer to the weakly coupled outer electron. If J^+ is not constant, the conservation of $\vec{J}$ requires a reorganization of both $\vec{J}^+$ and $\vec{j}$. The experimentally observed different spin polarization tendencies may therefore reflect different degrees of electron-core coupling for the $J_c = 3/2$ ($\Delta J = 0$) and the $J_c = 1/2$ ($\Delta J \neq 0$) series, respectively. The underlying interactions for the coupling of rotation and spin polarization may be weak, but as previous investigations [19] have shown, even a very small interaction such as the hyperfine coupling can strongly influence the photoelectron spin polarization. Once the corresponding levels are resolved energetically, one can expect to find an influence of even a weak coupling on the electron spin.

We thank N. A. Cherepkov and H. Lefebvre-Brion for stimulating discussions and valuable comments. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 216).

---

*Permanent address: Physico-Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia

[1] U. Heinzmann, Phys. Scr. **T17**, 77 (1987).
[2] J. Guo, A. Mank, and J. W. Hepburn, Phys. Rev. Lett. **74**, 3584 (1995).
[3] T. Huth-Fehre, A. Mank, M. Drescher, N. Böwering, and U. Heinzmann, Phys. Rev. Lett. **64**, 396 (1990).
[4] U. Fano, Phys. Rev. **178**, 131 (1969).
[5] A. Mank, M. Drescher, T. Huth-Fehre, N. Böwering, U. Heinzmann, and H. Lefebvre-Brion, J. Chem. Phys. **95**, 1676 (1991).
[6] A. Mank, M. Drescher, A. Brockhinke, N. Böwering, and U. Heinzmann, Z. Phys. D **29**, 275 (1994).
[7] H. Drescher, A. Brockhinke, N. Böwering, U. Heinzmann, and H. Lefebvre-Brion, J. Chem. Phys. **99**, 2300 (1993).
[8] Y. Zhu, E. R. Grant, and H. Lefebvre-Brion, J. Chem. Phys. **99**, 2287 (1993).
[9] H. Lefebvre-Brion, J. Chem. Phys. **93**, 5898 (1990).
[10] W. R. Hunter, Appl. Opt. **17**, 1259 (1978).
[11] U. Heinzmann, J. Phys. B **13**, 4353 (1980).
[12] N. A. Cherepkov, J. Phys. B **14**, 2165 (1981).
[13] N. A. Cherepkov (private communication).
[14] H. T. Wang, W. S. Felps, G. L. Findley, A. R. P. Rau, and S. P. Glynn, J. Chem. Phys. **67**, 3940 (1977).
[15] K. S. Haber, E. Patsilinakou, Y. Jiang, and E. R. Grant, J. Chem. Phys. **94**, 3429 (1991).
[16] R. G. Tonkyn, R. T. Wiedmann, and M. G. White, J. Chem. Phys. **96**, 3696 (1992).
[17] M. Büchner, G. Raseev, and N. A. Cherepkov, J. Chem. Phys. **96**, 2691 (1992).
[18] G. Raseev and N. A. Cherepkov, Phys. Rev. A **42**, 3948 (1990).
[19] E. H. A. Granneman, M. Klewer, and M. J. Van der Wiel, J. Phys. B **9**, 2819 (1976).