Experimental Angular-Resolved Photoelectron Spectroscopy of Free Oriented CH₃I Molecules

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A photoionization experiment on free oriented molecules in the gas phase has been performed. CH_3I molecules in a supersonic beam have been oriented with respect to the molecular axis parallel to an external field by use of an electric hexapole. The photoelectrons ejected by vacuum ultraviolet radiation in a region of a very weak field from the lone-pair orbital located at the iodine atom show a pronounced asymmetry depending on whether electrons are emitted parallel or antiparallel to the molecular axis.

Recent photoemission experiments with atoms,[1] molecules,[2] or solids[3] have shown that details of the photoionization dynamics can be obtained if the photoelectron spectroscopy studies are performed in an angular- and/or even spin-resolved manner. In molecular photoionization, however, still much detailed information was hidden because only randomly oriented molecules could be photoionized in previous gas-phase experiments. Theoretical investigations into the study of photoelectron emission of free oriented molecules became very important and have been successfully performed[4–8] after there was experimental evidence[9] that photoemission from molecules chemisorbed on a solid-state surface reflects the orientation of the molecules with respect to the surface. To close the gap between photoionization of randomly oriented molecules in the gas phase and of oriented molecules in the chemisorption requires experimental studies of the influence of the molecular orientation onto the molecular photoemission process. We present for the first time experimental results of an angular-resolved photoelectron spectroscopy study on free oriented molecules in the gas phase.

Diatomic closed-shell molecules with permanent electric dipole moment μ rotate perpendicularly to μ, so that their orientation requires enormous electric fields ($\sim 10^7$ V/cm) to overcome the rotational inertia of the molecules.[10–12] However, symmetric top molecules like CH_3I can have rotational states, where the rotational momentum J has a component parallel to μ, i.e., symmetric tops in these rotational states can be oriented in lower electric fields, which is a critical requirement in our photoionization experiment. The experimental technique corresponds to an "electrostatic Stern-Gerlach method"[10–14] with use of an electrostatic hexapole.

Figure 1 shows the schematic setup of the apparatus. The vacuum ultraviolet (VUV) lamp[15] and the cylindrical-mirror-analyzer electron spectrometer are necessary for photoelectron spectroscopy. The main parts of the source of oriented molecules are the supersonic beam source, the electrostatic hexapole, and the guiding field; in between a buffer field is placed. The interaction energy of a CH_3I molecule with an electric field $\mathbf{E}$ is[13]

$$W_{Stark} = -\mu E M_J K / J(J+1) = -\mu E \langle \cos\theta \rangle,$$

where θ is the angle between μ and $\mathbf{E}$, and J, K, and M_J are the rotational quantum numbers.[14] The force $\mathbf{G} = -\operatorname{grad} W_{Stark}$ onto the molecules in the inhomogeneous electric field of the hexapole separates molecules with different orientation of their axis relative to the local electric field direction spatially, i.e., for a given hexapole voltage V_0 only molecules with a specified degree of (local) orientation can pass the exit aperture. This local orientation is transformed into a spatially uniform orientation by an adiabatic transition from the hexapole into the quasihomogeneous guiding field (via the buffer field). In the guiding field the electric field strength drops slowly from 10 to 0.3 V/cm in the target region, where an angular-resolved investigation of the photoelectrons is feasible.

The main problems of the experiment are deorientation effects in the guiding field, caused by nonadiabatic transitions and nuclear-spin effects. It has been
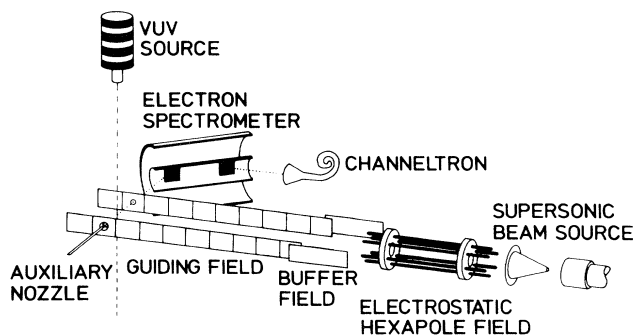

FIG. 1. Schematic diagram of the apparatus; the electrostatic field in the hexapole, in the buffer field, and at the end of the guiding field is $\leqslant 60$ kV/cm, 30 V/cm, and 0.3 V/cm, respectively.

shown[10] that the transitions from a hexapole into a guiding field, whose electric field was constant along the flight path of the molecules, are adiabatic, if the field is higher than 10 V/cm. As it is impossible to study photoelectrons angular resolved in such a strong electric field, we had to construct a guiding field with decreasing field strength. If the field drops too fast, nonadiabatic transitions take place. Deorientation by nuclear-spin effects occurs when the guiding field becomes so small that nuclear spin I and rotational angular momentum J are no longer decoupled. Instead of the quantum numbers M_J, which describe the orientation of the molecules relative to E, the quantum numbers M_F (projection $F = J + I$ on E) become good quantum numbers.[16] In our experiment, a rough estimation gives a rotational temperature of about 200 K, so that the most probable J is about 16. As $I = \frac{5}{2}$, 0, and $\frac{1}{2}$ for an I, C, and H atom, respectively, $J \gg I$ and the effect of nuclear spin is reduced, i.e., $M_F \sim M_J$.

CH_3I is expanded with 170 mbar through a 150-μm nozzle. The skimmer (diameter 0.9 mm) is placed 15 mm behind the nozzle. The hexapole (field strength up to 60 kV/cm) consists of six stainless-steel rods (5.5-mm diameter, 300-mm length, charged alternately to $\pm V_0$) placed on a circle with a 16.5-mm diameter. The central-beam stop (not shown in Fig. 1) has a diameter of 2.5 mm. At the end of the buffer field (length 110 mm, field strength ~ 30 V/cm) a divided aperture is placed, which prevents the penetration of the electric field of the guiding field, when the buffer field is grounded. The guiding field decreases proportional to $1/r$,[17] simulated by the use of twenty electrodes. In order to make the decrease as smooth as possible, these electrodes are connected by a graphite resistance layer. After a flight path of 360 mm in the guiding field, the molecules are ionized. The virtual exit aperture of the hexapole is formed by the overlap region of the VUV-light beam and the spectrometer
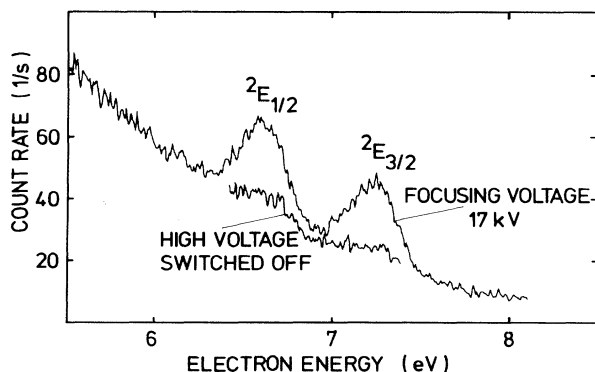
acceptance cone. A beam of unoriented, unfocused molecules can be produced by the auxiliary nozzle, as shown in Fig. 1.

Figure 2 shows a photoelectron spectrum of focused CH_3I molecules ionized by Ne I (16.67 and 16.85 eV) radiation. The two peaks correspond to the ionic final states $^2E_{3/2}$ and $^2E_{1/2}$, which result from the ionization of the lone-pair–type orbital $2e$, strongly localized on the iodine atom. The main part of the background is due to scattered light, and a smaller part from scattered CH_3I molecules. From the counting rates it can be estimated that some 10^{13} (focused molecules) s^{-1} cross the VUV-radiation beam.

In the experiment described in this Letter we have investigated whether there is an asymmetry for photoelectrons which are emitted parallel or antiparallel to the molecular axis. These two different molecular orientations with respect to the spectrometer are produced by a change in the polarity of the buffer and guiding fields (Fig. 3). If the methyl group is directed towards the spectrometer, a photoelectron current I^+ is detected; if the iodine atom is directed towards the spectrometer, a current I^- is detected. In order to take the energy dependence of the background (Fig. 2) into account, we have used a multichannel analyzer for these measurements.

Figure 4 shows the asymmetries I^-/I^+ measured for both spin-orbit components for Ne I (16.67 and 16.85 eV) and He I (21.22 eV) light. If the buffer field is switched on, the focused CH_3I molecules show a photoionization asymmetry of about 1.1 (filled data points). The smaller the focusing voltage V_0, the higher is the asymmetry effect (measured with Ne I light). Since for ideal orientation $\langle \cos\theta \rangle = -V_{th}/V_0$,[14] where angular brackets indicate expectation value and V_{th} is constant, the asymmetry I^-/I^+ shows the expected dependence on the focusing voltage. The asymmetries have been found to be identical within the experimental error bars for both spin-orbit components and independent of the photon energy. Apparatus-related asymmetries, which result from the low electric field in the target region, can be studied by measurement of the asymmetries of the randomly oriented molecules, which effuse from the aux-
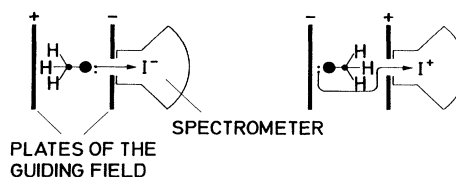
FIG. 2. Photoelectron spectrum of oriented and focused CH_3I molecules by use of Ne I VUV radiation.

FIG. 3. Schematic view of the molecular orientation with respect to the position of the electron spectrometer (for $\langle \cos\theta \rangle = -1$). I^- and I^+ are the photoelectron intensities measured behind the spectrometer exit slit.
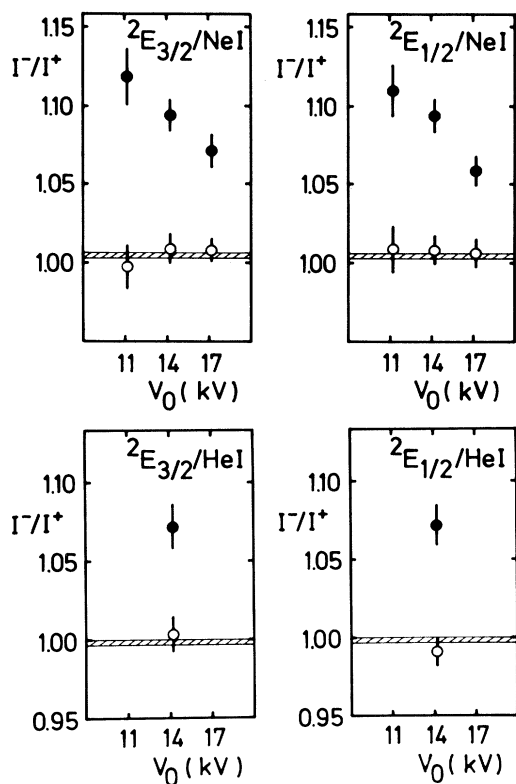
FIG. 4. Experimental results of the asymmetry I^-/I^+ of photoelectron intensities corresponding to the parallel and antiparallel emission with respect to the molecular axis as a function of the voltage in the hexapole. $E_{3/2}$, $E_{1/2}$ and Ne I, He I denote the quantum numbers of the molecular ionic state and the photon energies used, respectively. The filled and the open data points with the error bars correspond to the focused molecular beam with and without a buffer field, respectively. The dashed areas have been measured as apparatus-related asymmetries obtained by use of the molecular beam from the auxiliary nozzle shown in Fig. 1.

iliary nozzle into vacuum. They have been found to be between 1.004 ± 0.001 and 0.997 ± 0.001 (dashed areas in Fig. 4) for He I and Ne I light excitation, respectively (buffer field was on). These asymmetries are small because target region and spectrometer entrance are both on 0 V potential, i.e., the photoelectrons are first accelerated and then decelerated to their initial energy (or vice versa, respectively). Apparatus-related asymmetries, caused by discharge or other effects of the hexapole, can be studied by grounding the buffer field, which causes a randomization of molecular orientation.[18] The asymmetries measured in that way vanish (open data points in Fig. 4).

From the fact that the asymmetries of focused molecules show the expected dependence on V_0, if the buffer field is on, and the fact that apparatus-related asymmetries are found to be negligible, it must be

concluded that electrostatically oriented molecules do not lose their orientation even in weak electric fields, if the guiding field is appropriate. Unfortunately we do not have yet a calibrated method to analyze experimentally the degree of molecular orientation quantitatively. To do that in the future we have to start with additional experiments using linearly polarized radiation or spin-polarized electrons. Instead of that we have estimated the orientation of the molecules, using a ray-tracing procedure.[10] For $V_0 = 14$ kV, upper (lower) limits of 0.28 (0.33) for $- \langle \cos\theta \rangle$ have been obtained [0.24 (0.28) and 0.34 (0.40) for 17 and 11 kV, respectively], where the overbar indicates the average in the ray-tracing procedure. Because small deorientation effects in the guiding field cannot be excluded, the real degree of orientation at the phototarget may be still smaller. When we compare this degree of orientation with the highest-asymmetry ratio of 1.12 ± 0.02 found, the forward-backward photoelectron emission asymmetry parallel to the molecular axis must be a pronounced effect for a complete orientation of the molecules. As the asymmetry for He I and Ne I radiation has been found to be the same within the experimental uncertainty, it may be caused by an initial-state effect which reflects the anisotropic spatial distribution of the electrons in the lone-pair orbital. The observed asymmetry can only be caused by odd harmonics in the photoelectron angular distribution.

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