# Elastic Electron Scattering from $CH_3I$ Molecules Oriented in the Gas Phase

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(Received 25 February 1992)

A novel experiment on elastic electron scattering from free, spatially oriented molecules has been performed. $CH_3I$ molecules state selected by an electrostatic hexapole lens were oriented in a homogeneous electric field. The differential scattering cross sections were measured at an electron energy of 1 keV in the angular range of 4°–14° with the orientation switched on and off. From these data the orientation-dependent contribution to the molecular interference was determined. The results show a distinct oscillatory pattern as a function of momentum transfer as predicted by theory.

PACS numbers: 34.80.Bm, 35.20.Dp, 35.80.+s

In gas-phase electron diffraction the geometrical structures of unoriented molecules can be determined very precisely from the interference of the various atomic scattering centers [1–3]. However, such data sets are inherently *one dimensional,* due to complete averaging over the randomly distributed orientations of the molecules in the sample gas. Therefore, the structural results obtained by a multiparameter fitting procedure can contain strongly correlated parameters. On the other hand, if the molecules are spatially oriented in the laboratory frame, the scattering distributions contain *three-dimensional* information similar to results obtained from x-ray diffraction of single crystals. Consequently, by recording the diffraction patterns from oriented molecules, not only the absolute values of the intramolecular spacings $|\mathbf{r}_{ij}|$ and vibrational amplitudes $|\mathbf{l}_{ij}|$ between the atoms $i$ and $j$ but also the individual $x$, $y$, and $z$ components of these quantities and, therefore, the molecular bond angles may be extracted in a direct way. It has been pointed out in a recent theoretical study that a real-space image can be reconstructed from gas-phase electron diffraction data for state-selected, oriented molecules by special Fourier transform inversion techniques [4].

A strong orientational dependence of the elastic differential scattering cross sections was first predicted by calculations in 1989 for molecules assumed to be rigidly fixed in space [5,6]. Kohl and Shipsey then extended the calculations to fully rotating symmetric top molecules in selected quantum mechanical rotational states oriented or aligned in an electric field [4]. A general theory for the discussion of spin-dependent elastic electron scattering from oriented molecules has also been derived [7]. The theoretical studies based on the independent atom model (IAM) [4–6] showed that sizable effects might be observed. We present here the first experimental results for electron scattering from free oriented molecules.

Axis orientation of polar symmetric top molecules [8] in the gas phase can be achieved in molecular beam experiments via the linear Stark effect by using an electrostatic hexapole lens and orientation field plates (for a review, see Refs. [9,10]). The hexapole acts as a state selector focusing only molecules in states that exhibit a positive Stark effect. This method has the advantage that although the field strengths within the hexapole are high the oriented molecules can be transferred to a weak-field region by adiabatic transition through a subsequent guiding field. This technique was used with good success for photoionization studies of oriented $CH_3I$ molecules [11]. The electron scattering experiments reported here have also been performed in a low-field region. The term "orientation" is used here to describe the orientation of the molecular dipole moment $\mathbf{p}$ with respect to an external electric field $\mathbf{E}$ (angle $\Theta$). Symmetric top molecules in specific rotational states $|J,K,M\rangle$ with $\langle\cos\Theta\rangle = KM/J(J+1) \neq 0$ are oriented and the rotational probability distribution $P_{JKM}(\cos\Theta)$ can be calculated quantum mechanically [12]. ($K$ and $M$ are the quantum numbers of the projection of the total angular momentum $J$ on the molecular symmetry axis and on the electric field direction, respectively.)

Apart from the usual scattering angle $\vartheta$ between the momenta $\mathbf{k}_0$ and $\mathbf{k}$ of incident and scattered electrons, respectively, the scattering process considered here depends in addition on the orientation of the electric field direction with respect to the scattering plane described by the polar angle $\Theta_s$ and the azimuthal angle $\chi_s$; see Fig. 1. The elastic differential cross section in the IAM for

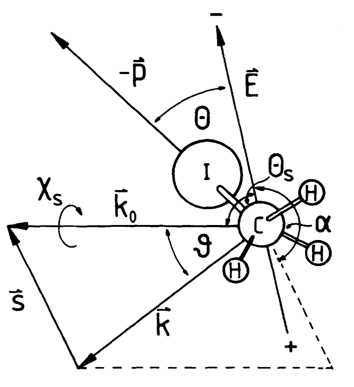

FIG. 1. Schematic of the scattering geometry illustrating the relative orientations of the vectors $\mathbf{E}$, $\mathbf{p}$, $\mathbf{k}_0$, $\mathbf{k}$, and $\mathbf{s}$.

oriented (or aligned) molecules in a specific rotational state $|J,K,M\rangle$ was derived in Ref. [4]. It can be written as the sum of the electron cross section for randomly oriented molecules (indicated by the subscript $R$) [13] and of a new interference term $M_{JKM}$ containing additional contributions originating from the molecular orientation:

$$\left(\frac{d\sigma}{d\Omega}\right)_{JKM}=\left(\frac{d\sigma}{d\Omega}\right)_R+M_{JKM}(\Theta_s,\vartheta,\chi_s)\,. \tag{1}$$

$M_{JKM}$ is a function of the scattering angle $\vartheta$, the azimuthal angle $\chi_s$, and the angle $\Theta_s$ and is given by

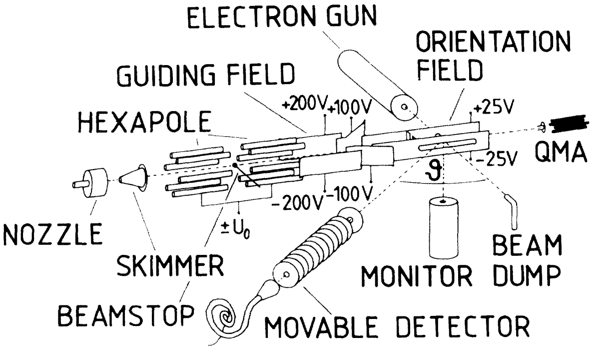

FIG. 2. Schematic view of the apparatus.

$$M_{JKM}(\Theta_s,\vartheta,\chi_s)=(2J+1)\sum_{i<j}|f_i||f_j|\sum_{n=1}^{2J}C_{JKMn}\,\mathrm{Re}\{\exp[i(\eta_i-\eta_j)]F_{nij}(\mathbf{s})\}\,, \tag{2}$$

where the functions $F_{nij}(\mathbf{s})$ are defined as

$$F_{nij}(\mathbf{s})=2(2\pi)^2 i^n P_n(\cos\alpha)\,\Omega_V(P_n(\cos\beta_{ij}^0)j_n(sr_{ij}^0)) \tag{3}$$

in terms of the Legendre polynomials $P_n$ and the spherical Bessel functions $j_n$. Here, $f_i$ and $\eta_i$ are the direct scattering amplitudes and phases of atom $i$, respectively, $C_{JKMn}$ are expansion coefficients [12], $s=2k\sin(\vartheta/2)$ is the transferred momentum, $\Omega_V$ is a differential operator for the vibrational damping, and $\alpha$ is the angle between the electric field $\mathbf{E}$ and the transferred momentum $\mathbf{s}$ which is related to the other angles by

$$\cos\alpha=\frac{\sin\vartheta\sin\Theta_s\cos\chi_s+(1-\cos\vartheta)\cos\Theta_s}{2\sin(\vartheta/2)}\,, \tag{4}$$

as derived and discussed by Kohl and Shipsey [4]. The parameter $\beta_{ij}^0$ in Eq. (3), with

$$\cos\beta_{ij}^0=z_{ij}^0/r_{ij}^0\,, \tag{5}$$

leads directly to the bond angles in terms of equilibrium distances. With our molecular beam apparatus an ensemble of quantum states of oriented molecules is produced in the scattering region. The individual states denoted by $i=|J,K,M\rangle$ are populated with a relative population fraction $w_i$. Hence, the intensity $I$ of electrons scattered into a solid angle $\Delta\Omega$ can be written as

$$I(\Theta_s,\vartheta,\chi_s)=\sum_i w_i I_i+I_B=I_{RB}+I_0 N\sum_i w_i M_i\Delta\Omega\,. \tag{6}$$

$I_0$ is the current density of the electron beam, $N$ is the number of target molecules, $I_B$ is the background scattering intensity due to the residual gas, and $I_{RB}$ is the sum of $I_B$ and the orientation-independent part of the contribution from the target molecules.

The apparatus is shown in Fig. 2. A cw supersonic molecular beam with a translational energy of 100 meV is generated by expanding $CH_3I$ through a 0.15-mm-diam nozzle at a stagnation pressure of 250 mbar into vacuum ($p=6\times10^{-5}$ mbar) using a skimmer of 0.4 mm diam. The beam passes through the hexapole assembly (6-mm-diam entrance aperture located 20 cm behind the nozzle, $p\leq5\times10^{-8}$ mbar). It consists of six chromium-plated brass rods of 6 mm diam on a circle of 12 mm charged alternately to $\pm U_0$ and is divided into two equal parts 0.25 m in length. A central beamstop (2 mm diam) blocks the direct beam preventing molecules with ($\langle\cos\Theta\rangle_i=0$) from reaching the target region. Molecules in states exhibiting a positive Stark effect ($\langle\cos\Theta\rangle_i<0$) can be focused into the target region 0.52 m behind the hexapole. The beam passes through a guiding field ($U=\pm200$ V, length $=23$ cm) to avoid loss of molecular orientation by mixing of the $M$ quantum states (Majorana flops). Behind the hexapole exit aperture the molecules are transferred via an adiabatically decreasing guiding field ($U=\pm100$ V) [11] into a final homogeneous orientation field ($U=\pm25$ V, field strength $E=\pm50$ V/cm) in the scattering chamber [$p\leq(2-3)\times10^{-8}$ mbar]. A slit of 2 mm width mounted inside the orientation field 5 cm in front of the scattering region defines the scattering volume.

The electron beam (1 keV, 10 $\mu$A) produced by a telefocus electron gun [14] travels perpendicular to the molecular beam and parallel to the orientation field. It passes through an entrance hole (4 mm diam) and an exit slit (4 mm height, 10 cm length) centered in the orientation field plates. This way, elastically scattered electrons in a range of $\vartheta=\pm60°$ can be detected. The orientation field plates are mounted inside a grounded metallic frame with similar openings to minimize stray fields. The detector, consisting of a retarding field analyzer [15] and a channeltron, can be rotated in the scattering plane by means of a stepper motor. With a second detector at a fixed scattering angle, changes in the intensity of the electron beam and in the background pressure are recorded. The molecular beam was monitored by means of a quadrupole mass analyzer mounted behind the orientation field. The data acquisition is controlled by a personal computer.

Relative differential cross sections for scattering angles of 4°–14° were measured with the field polarities such that the molecules were oriented preferentially parallel (field orientation angle $\Theta_s = 0°$) or antiparallel ($\Theta_s = 180°$) to the electron beam. In this geometry electron scattering is independent of the azimuthal angle $\chi_s$, since $\mathbf{k}_0$ and the direction of reference for the molecular orientation, $\mathbf{E}$, are parallel. At each scattering angle the intensities $I(\Theta_s, \vartheta)$ were measured for $\Theta_s = 0°$ ($CH_3$ group pointing preferentially towards the incident electrons) and for $\Theta_s = 180°$ (all field polarities reversed). By switching off *only* the guiding fields, the orientation was turned off without affecting the electron scattering and $I_{RB}(\Theta_s, \vartheta)$ was determined for each case. The orientation field acts as a weak lens for the primary and scattered electrons. Hence the intensities $I_{RB}$ were not identical for the two polarities of the field, because the current densities of the electron beam were different. This apparatus asymmetry varies from 0.05 for small momentum transfer $s$ to almost zero for larger values of $s$.

To determine only the intensity contribution from randomly oriented target molecules,

$$I_R(\Theta_s, \vartheta) = c(\Theta_s, \vartheta) I_{RB}(\Theta_s, \vartheta),$$

the background from residual gas scattering was measured with the hexapole voltages off (no molecular beam in the target region) and subtracted from $I_{RB}(\Theta_s, \vartheta)$. $c$ was found to be equal to $0.14 \pm 0.03$, independent of the angles $\Theta_s$ and $\vartheta$. In order to obtain a direct measure of the orientational molecular interference contribution, the relative change of the elastic differential cross section was determined according to

$$\Delta_\sigma(\Theta_s, \vartheta) = \frac{I(\Theta_s, \vartheta) - I_{RB}(\Theta_s, \vartheta)}{I_R(\Theta_s, \vartheta)}$$

$$= \left[ \sum_i w_i M_i(\Theta_s, \vartheta) \right] \Big/ \left( \frac{d\sigma}{d\Omega} \right)_R . \qquad (7)$$

In contrast to the usual determination of the molecular interference for unoriented molecules [1-3], $\Delta_\sigma$ is independent of a model; furthermore, the background intensity, the current density of the electron beam, the solid angle to the detector, and the apparatus asymmetry cancel. Figure 3 (top and center) shows the results [see Eq. (7)] as a function of transferred momentum for both orientations. (Data at positive and negative values of $\vartheta$ have been averaged; each point represents ca. 1 h of data accumulation.) At a hexapole voltage of ±7 kV the data for the deviation from the cross section of unoriented molecules show similar oscillations but with larger amplitude for parallel than for antiparallel orientation. To verify that the results are independent of the apparatus asymmetry, $\Delta_\sigma$ was also measured with the hexapole voltage turned off [for $\Delta_\sigma(\Theta_s = 0°)$, see Fig. 3, bottom]. It is zero within error, as required.

In accordance with Refs. [16-18] a rotational temperature of ca. 70 K has been estimated for our neat $CH_3I$ beam. The population fractions for the ensemble of

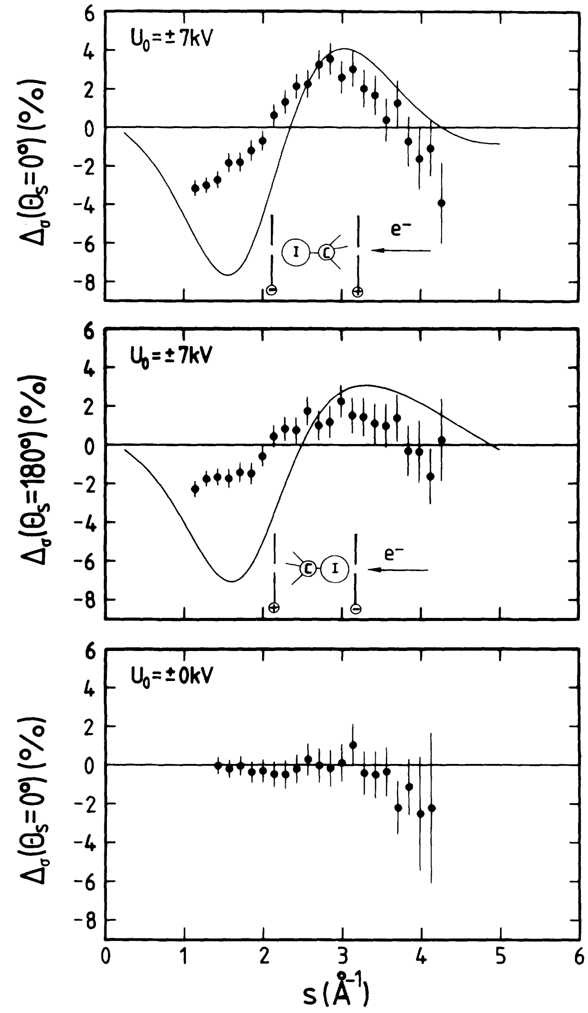

FIG. 3. Deviation of the elastic differential cross section for oriented molecules from that of unoriented molecules obtained using Eq. (7) at 1 keV electron energy (hexapole voltage $U_0$ as indicated). The data points (±1$\sigma$ statistical error) are for the field orientation angles $\Theta_s = 0°$ (top) and $\Theta_s = 180°$ (center), and for molecular beam switched off (bottom). The full curves represent the theoretical result for $T_{\rm rot} = 70$ K.

states focused into the target region were calculated for the expansion conditions of the molecular beam by a ray-tracing procedure for a given hexapole voltage $U_0$ and molecular rotational temperature $T_{\rm rot}$ [19] neglecting nuclear hyperfine coupling. At $T_{\rm rot}$ between 30 and 200 K and at $U_0 = \pm 7$ kV the average degree of orientation $\langle \cos\Theta \rangle$ was calculated to lie between 0.26 and 0.25. For these ensembles the mean interference term $\overline{M}(\Theta_s, \vartheta) = \sum w_i M_i$ [Eq. (2)] and $\Delta_\sigma(\Theta_s, \vartheta) = \overline{M}(\Theta_s, \vartheta)/(d\sigma/d\Omega)_R$ [Eq. (7)] were determined using the IAM. For simplification, the damping $\Omega_V$ was set to unity. In order to compare $\Delta_\sigma$ with the experimental data, $\overline{M}$ and $(d\sigma/d\Omega)_R$ were convoluted with the transmission function of the detector (angular resolution $\Delta\vartheta = \pm 1.1°$). This convolution as well as the variation of $T_{\rm rot}$ caused only small alterations ($<5\%$ and $<20\%$, respectively) of the theoretical curves for $U_0 = \pm 7$ kV. As seen from Fig. 3, the shapes of the theoretical curves at $T_{\rm rot} = 70$ K and the experimental data are similar. In this comparison of *ratios* only effects which are different for oriented and unoriented molecules play a role. Above $s = 2$ Å$^{-1}$ the theory predicts a larger maximum for parallel orientation (ca. 4%) than for antiparallel orientation (ca. 3%), which is compatible with the experiment. On the other hand, there is a deviation for the minima at small momentum transfer where the theoretical amplitude is ca. (7-8)%. Furthermore, the zero crossings of $\Delta_\sigma$ for both orientations seem to be shifted by 1°-2° to larger angles as compared to the experiment. These remaining discrepancies cannot be fully resolved at present; they are attributed mainly to the limited knowledge of the rotational state distributions (which were only calculated) and the approximations made in the theory based on the IAM. Several improvements to the experiment are planned to obtain a more sensitive test of the theory in the future.

In conclusion, we have reported experimental evidence of a new molecular interference contribution to the electron diffraction pattern present when the scattering molecules are oriented. The fair agreement of the experimental data with the theory of Kohl and Shipsey [4] applied to the state mixture of $CH_3I$ molecules is encouraging in view of future development of this method for molecular structure studies.

The authors thank Professor U. Heinzmann for many stimulating discussions and his continuous interest and very generous support. We are also grateful to Dr. G. H. Fecher, Professor D. A. Kohl, and Dr. N. Müller for valuable suggestions and discussions. A.M. and M.F. are grateful for the hospitality at the Physics Department received during their stay at the University of Bielefeld. Financial support of the Deutsche Forschungsgemeinschaft (SFB 216) for the project and the Fulbright Commission (for A.M.) is gratefully acknowledged.

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