Inelastic Scattering of CO with He: Polarization Dependent Differential State-to-State Cross Sections

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ABSTRACT: A joint theoretical and experimental study of state-to-state rotationally inelastic polarization dependent differential cross sections (PDDCSs) for CO (ν = 0, j = 0, 1, 2) molecules colliding with helium is reported for collision energies of 513 and 840 cm⁻¹. In a crossed molecular beam experiment, velocity map imaging (VMI) with state-selective detection by (2 + 1) and (1 + 1) resonance enhanced multiphoton ionization (REMPI) is used to probe rotational excitation of CO due to scattering. By taking account of the known fractions of the j = 0, 1, and 2 states of CO in the rotationally cold molecular beam (Trot ≈ 3 K), close-coupling theory based on high-quality ab initio potential energy surfaces for the CO–He interaction is used to simulate the differential cross sections for the mixed initial states. With polarization-sensitive 1 + 1′ REMPI detection and a direct analysis procedure described by Suits et al. (J. Phys. Chem. A 2015, 119, 5925), alignment moments are extracted from the images and the latter are compared with images simulated by theory using the calculated DCS and alignment moments. In general, good agreement of theory with the experimental results is found, indicating the reliability of the experiment in reproducing state-to-state differential and polarization-dependent differential cross sections.

1. INTRODUCTION

Rotational excitation of diatomic molecules by collisions with atoms has been studied in intricate detail over the past few years, particularly for collisions of argon with the molecule NO,1–3 where state-to-state measurements of collision-induced orientation and alignment of the NO final rotational angular momentum as a function of scattering angle has been determined. Recently, these measurements on NO–Ar have been extended to study the effects of preorientation of the NO molecular axis before collision.4 Because these are nearly “perfect” experiments where all reactant and product variables are controlled, they form a suitable challenge for ab initio quantum theory. In practice, the systems studied so far are simple enough that theory at present has proven to be more accurate than experiment, even for the open-shell NO molecule. In this case, imperfections in experiment, noted as deviations from theory, can then be identified, accounted for, and/or improved. This bootstrap process is necessary to prepare for experimental studies of scattering processes involving more than 3–4 atoms, which offer significant challenges for a fully quantum theoretical treatment. In this direction, encouraging agreement has already been found between advanced experiment and semiclassical or reduced dimensional quantum theory for the systems OH–NO,5 H₂O–H₂,6 NH₃–H₂,7 and CH₃–N₂,8 for example.

In this paper we describe a joint experimental and theoretical study at a similar level of detail as for the recent studies on NO–He/Ar, but now for collisions of He with the closed-shell molecule CO. There is a long history of CO–He inelastic scattering studies, as outlined later in this section. An experimental study with angular momentum polarization-sensitive state-selective detection of CO is, however, far more challenging than for NO because the excited electronic states that can be used as a resonance step for CO lie deep in the vacuum ultraviolet (VUV). Although CO inelastic scattering is less challenging for ab initio full quantum theory than NO, prediction of state-to-state polarization-dependent differential scattering cross sections (PDDCS) for CO–He elastic and inelastic scattering, as described here, has not been reported.

Two ab initio potential energy surfaces are compared in this paper, one from the more recent study of Peterson et al.9 named CBS+corr, and the other a symmetry-adapted perturbation theory (SAPT) potential from 1997 taken from Heijmen et al.10 Both potentials have been proven to be highly...
accurate in simulating the collision energy dependence of integral cross sections for low-energy scattering resonances of CO + He.\(^{11}\)

In our experiment we utilize two different laser ionization detection schemes with resonance enhanced multiphoton ionization (REMPI) of CO in the \((2 + 1)\) and \((1 + 1')\) configurations, couple this with velocity map imaging (VMI) detection,\(^6,\) and measure (PD)DCSs describing collisions of CO \((j = 0, 1, 2)\) with helium at collision energies 513 and 840 cm\(^{-1}\). Here, \(j\) refers to an initial rotational state of CO whereas \(j'\) refers to a nascent state populated by collision. \((2 + 1)\) REMPI detection of CO via the E-state\(^5\) is highly efficient, convenient, and for our conditions, polarization insensitive, and thus useful for extracting the pure DCS. We have shown in a recent paper\(^7\) that the \((1 + 1')\) detection method for CO–Ar collisions is polarization sensitive and produces high-resolution images. Taking advantage of the sharp and polarization-sensitive images, we demonstrated a simple scheme for extracting the polarization moments describing collision-induced alignment for the CO–Ar (final CO state \(j' = 9\)) system directly from the measured VMI images. We test this method here for CO–He collisions for a range of final rotational \((j')\) states of CO.

CO–He has served as a benchmark for energy-transfer dynamics, and also as a model for the CO–H and CO–H\(_2\) collision systems. Earlier work has been done to identify the key aspects of the potential energy surface. Early molecular beam experiments on CO–He were reported by Butz et al. in 1971,\(^{15}\) and Nerf et al. in 1975 presented the first experimental evidence of sensitivity to anisotropy of the CO–He potential.\(^{16}\) Antonova et al.\(^7\) measured relative state-to-state integral cross sections for rotational excitation of CO in collision with helium at collision energies of 583 and 720 cm\(^{-1}\). They compared their experimental data with results from two high-quality potential energy surfaces, with the \(ab\) initio SAPT surface of Heijmen et al.\(^{10}\) and with the XC(\(\text{fit}\)) surface of LeRoy et al.\(^{18}\) and found better agreement for the SAPT surface.\(^{10}\) Lorenz et al. measured state-to-state differential cross sections for rotational excitation of CO in collision with Ne at a collision energy near 511 cm\(^{-1}\), and they have compared their experimental data with results based on the CCSD(T) surface of McBane and Cybulski and the surface of Moszynski et al.\(^{19–21}\) In 2004, Smith et al.\(^{22}\) reported state-to-state rotational transition rate constants for CO–He obtained from infrared double resonance measurements and scattering calculations based on the SAPT potential of Heijmen et al.\(^{10}\) Their work provided a nice demonstration of the quality of the SAPT potential. Even better \(ab\) initio CO–He potentials were calculated more recently and tested against experimental data in scattering calculations by Peterson and McBane.\(^9\) In the present article comparison of the differential cross sections from our measurements with the calculations on the SAPT potential\(^{10}\) and the best potential of Peterson et al.\(^9\) demonstrate the accuracy of these potentials.

Carbon monoxide is of high astrochemical relevance as the second most abundant molecule in the universe after molecular hydrogen. Radiation emitted by CO is commonly used as a tracer to extract astrophysical parameters, as rotational transitions of the asymmetric molecule CO provide the best means to determine the physical conditions of the interstellar medium. Many models of the processes occurring in such environments are based on the assumption of local thermodynamic equilibrium (LTE). However, when hot stars, low-density chromospheres, and coronae of solar-type stars are investigated, the LTE approximation breaks down and non-LTE modeling is required.\(^{23–25}\) In this case, successful modeling of the observed CO spectral lines requires the knowledge of accurate collision rate coefficients of CO with its dominant collision partners: He, H\(_2\), H, and electrons.\(^{24,26}\) Rate coefficients are commonly obtained from theoretical calculations, the quality of which must be tested by experiment. Differential cross sections (DCS) measured in crossed-molecular beam experiments have been shown to provide the most stringent test for state-of-the-art theoretical calculations.\(^{27,28}\)

To introduce the energetics of the CO–He imaging experiment, a Newton diagram and a typical scattering image for the \(j' = 7\) final state of CO is shown in Figure 1. The images are two-dimensional “crushed” projections of the three-dimensional velocity spheres, having the form of a ring displaced from the center of the image (zero velocity position) by the velocity of CO relative to the center-of-mass velocity. The variation of the intensity around the ring provides the nature of scattering, e.g., forward or backward scattering, which in turn reveals the nature of the interaction between the colliding species.

2. EXPERIMENTAL METHOD

The data were collected in a crossed molecular beam machine with a variable beam crossing angle and REMPI ionization of the scattered products with velocity map imaging detection as shown schematically in Figure 2. The basic apparatus was described in ref 29; details specific to the \(1 + 1'\) REMPI measurements are given here.

We used two skimmed supersonic beams, one of neat helium produced from a Nijmegen pulsed valve,\(^{10}\) and the other of 2% CO seeded in argon produced from a second Nijmegen pulsed valve. Backing pressure for the expansion was 3 bar for both
molecular beams. The pulse duration of both valves at the crossing point is about 50 µs. The source chamber that houses the secondary beam (He) was differentially pumped and the molecular beam passes through a skimmer of aperture diameter 2.5 mm positioned 3 cm away from the nozzle. The primary molecular beam source was mounted in the differentially pumped rotatable chamber positioned 7 cm from the skimmer of aperture diameter 2.5 mm. All vacuum chambers were pumped by turbo molecular pumps. The laser and molecular beams were coplanar and parallel to the imaging detector face and were optimally aligned to ensure the best signal.

Rotational populations of the parent CO/Ar beam were obtained from the (2 + 1) REMPI spectrum of the E′Π → X′Σ+ transition of CO. Similar to the results of Antonova et al., the population of j = 0 was about 65% and of j = 1 about 33%, corresponding to a rotational temperature of 3 K, and a small fraction of higher states with a close to thermal distribution are present. By comparing the PGOPHER simulated spectrum with the experimental one, we can determine the most favorable REMPI line positions for detection of higher rotational states, which is the prerequisite information for state-to-state inelastic scattering studies.

Under collision conditions, depletion of the CO j = 0 ground state was measured to be less than 10%, which should ensure a single inelastic collision. The scattered product was ionized using either (2 + 1) or (1 + 1′) REMPI, and the ionic velocity sphere extracted by a velocity map imaging electrostatic lens. After 85 cm free flight along the time-of-flight tube, the 3-D ion sphere was crushed onto 2-D detector, which is read by a CCD camera. Application of time gating at the detector enables selection of the required mass and filters out background ions of other mass. The laser and both molecular beams were operated at 10 Hz. Typically, 20–50 000 laser shots were averaged for each image, under interleaved conditions with and without the He beam in time overlap with the CO beam. The second condition was used for background subtraction; difference images are taken when the final-state population in the parent is significant and overlaps the scattered-in final-state image. This subtraction method is not ideal; it leads to problems, especially in the forward scattering region, as discussed later in the text. The laser frequency was fixed during each image collection, rather than scanning the wavelength over the full width of the Doppler profile of the REMPI transition (0.07 cm⁻¹ for inelastic scattering of CO from He), because the laser bandwidth with both (2 + 1) and (1 + 1′) REMPI is ≈0.1 cm⁻¹. For (2 + 1) REMPI the ≈2 mJ energy per pulse power broadening of the transitions was also sufficient to make Doppler scanning unnecessary.

For (2 + 1) REMPI on the E′Π–X′Σ+ transition, well-resolved and strong S-branch transitions around 215 nm were used for data collection. The laser wavelengths were generated by frequency tripling the output of a tunable pulsed dye laser (Fine Adjustment) operating with DCM dye using two BBO crystals. The dye laser was pumped by a Nd:YAG laser (Continuum Surelite) operating at 532 nm and with 10 Hz repetition rate. Ultraviolet (UV) laser energies were typically ≈2 mJ per pulse in pulses of duration 4–6 ns. The probe beam was focused with a 20 cm lens onto the intersection region of the molecular beams.

For (2 + 1) REMPI of CO the E′Π state was used as the resonant state instead of the commonly used B′Σ+ state where the low-j levels are overlapped. Detection on the S-branch of the E′Π state should in principle be polarization sensitive but repeated measurements (under the same experimental conditions as (1 + 1′) REMPI) did not reveal any sensitivity to the laser polarization. Due to the low ionization efficiency and small probe volume, it was necessary to use 2 mJ laser pulse energy, which is likely to be too high to retain polarization sensitivity. Antonova et al. used 100 µJ per pulse, for example, and estimated that the maximum polarization effect in the integral cross section for CO–He scattering with E-state detection was less than 10%.

Experiments employing (1 + 1′) REMPI of CO were described briefly in ref 14. Radiation at ≈249 nm tun resonant with the two-photon Sp6 → Sp6p[1/2] transition at 80 119 cm⁻¹ in Xe was combined in a cell containing 30 mbar Xe with tunable radiation around 650 nm to generate tunable 154 nm light by difference frequency generation. This VUV light is resonant with the CO A′Π–X′Σ+(v = 0) transition. For simplicity we label the ionization process as (1 + 1′) REMPI. Although the 154 nm light drives the resonant excitation, the process driving ionization of the A-state is not yet identified. Analysis of the size and shape of the parent CO+ beam spot shows that ionization is close to threshold (i.e., ion recoil is small), indicating that ionization occurs by the combination of 248 nm + 650 nm photons. A photoelectron study is presently underway to better identify the ionization process. The collision energy was 840 cm⁻¹ for the geometry used in the (1 + 1′) REMPI detection experiments. This is higher than in the (2 + 1) REMPI detection experiments due to a different mounting of the pulsed valves, which led to a higher equilibrium temperature after warming up. The collision energy was estimated for both REMPI detection methods by combining data both from the initial beam velocities and from the size of the images as a function of the final rotational state j′.
The PGOPHER program was used to fit the CO \( A \rightarrow X (1 + 1') \) REMPI transition, which shows P, Q, and R branches of similar intensities, and (as with the \((2 + 1)\) REMPI spectrum) a rotational temperature of \(\approx 3\) K. This similarity indicates that the ionization step in the \((1 + 1')\) process does not significantly perturb the spectrum. The measured images for the same \(j'\) are different when a P, R, or Q branch transition is used. For the same transition branch the images differ with H (VUV laser polarization direction in the scattering plane) versus V polarization where the VUV polarization is directed perpendicular to the scattering plane, along the time-of-flight axis, as shown later. As described in ref 14, all H and V polarization images were obtained for Q-branch transitions.

The raw H and V images were first converted from density to flux using the IMSIMM program, although for the polarization analysis method this was not essential. The asymmetry in the raw images disappears to a large extent upon density to flux correction. Because the effective angular resolution varies widely with scattering angle, the images still do not look fully symmetric after correction. The density to flux correction is a secondary effect in that at any scattering angle the alignment moments are obtained by differences divided by the DCS. For each \(j'\) final state, two angular distributions were extracted from the H and V images by integrating over the outside annulus of the image, or over a stripe through the middle of the image along the initial relative velocity vector, as described in ref 14. This yields four polarization angular distributions: HIP, horizontal in-plane; VIP, vertical in-plane; HOOP, horizontal out-of-plane; and VOOP, vertical out-of-plane polarization.

An important difference between the present CO–He experiment and the CO–Ar experiment described in ref 14 is the direction of laser propagation, \(k_{\text{lab}}\). Using the standard reference frame as sketched in Figure 3, the z axis is parallel to the initial relative velocity vector \(k\), \(x\) is the scattering plane containing \(k\) and the product relative velocity vector \(k'\), and the y axis is parallel to \(k \times k'\). Using linearly polarized light, the electric field of the laser can be directed either along \(z\) (labeled horizontal or H polarization) or along the ion time-of-flight axis \(y\) (vertical, V polarization) when \(k_{\text{lab}}\) is directed along the x axis. In the laboratory frame, \(k_{\text{lab}}\) is the same as in the CO–Ar experiment, fixed at an angle of 45° with the CO initial velocity vector \(v_{\text{CO}}\). In the CO–Ar case, this angle and the angle of 85° between the CO and Ar beams, cf. Figure 1, implied that the laser beam was perpendicular to the initial relative velocity vector \(k\). Also in the CO–He experiments the CO and He beams cross at an angle of 85° and for the collision energy of 840 cm\(^{-1}\), where the CO final-state detection is polarization sensitive, the velocities of CO and He are such that the angle between \(k_{\text{lab}}\) and \(k\) is 120°. The implications of this different geometry are discussed later in the text.

### 3. THEORETICAL METHOD

Integral, differential, and polarization-dependent differential state-to-state cross sections for CO–He collisions were computed using the quantum close-coupling (CC) method. The most accurate potential from the work of Peterson et al., CBS+corr, was used; the SAPT potential was taken from Heijmen et al. Both potentials were calculated as full three-dimensional CO–He potentials; we used the two-dimensional potentials obtained by averaging them over the ground-state vibrational wave function of CO. The CO molecule was then treated as a rigid rotor, with the experimental rotational constant \(B_0 = 1.9225\) cm\(^{-1}\). The 2D CO–He potential is a function of the Jacobi coordinates \(R\), the length of the vector \(R\) pointing from the CO center of mass to the He nucleus, and \(\gamma\), the angle between \(R\) and the CO bond axis (\(\gamma = 0\) for linear CO–He).

The coupled channel equations were solved with the renormalized Numerov propagator, with \(R\) ranging from 3 to 50 \(a_0\) with a step size of 0.06 \(a_0\). The potential was expanded in normalized Legendre polynomials \(P_j(\cos \gamma)\) with \(\lambda\) running from 0 to 12. The \(R\)-dependent expansion coefficients were computed by 13-point Gauss-Legendre quadrature in the angle \(\gamma\). The channel basis consisted of functions for CO with a maximum value of \(j = 30\); total angular momenta up to \(J_{\text{lab}} = 90\) were included. With these parameters all of the calculated inelastic cross sections are converged to better than 1%. Both integral and differential cross sections were computed for transitions from initial states with \(j = 0, 1, 2\) to all final states up to \(j' = 15\). The cross sections calculated for the different initial CO \((j)\) states were weighted by the populations of these states in the mixture to compare the calculated values with the experimental data. Because of the spread of about ±40 cm\(^{-1}\) in the experimental collision energies of 513 and 840 cm\(^{-1}\), we computed the (PD)DCSs at 473, 513, and 553 cm\(^{-1}\) and at 800, 840, and 880 cm\(^{-1}\), and averaged the results with a weight ratio of 25:50:25%.

### 4. RESULTS AND DISCUSSION

#### 4.1. Theoretical Results

The potentials of Heijmen et al. and Peterson et al. used in the scattering calculations are compared in Figure 4 by showing the main coefficients in the

![Figure 3](image1.png) Definition of the laboratory frame coordinate system for the He–CO scattering process. See text and Figure 2 of ref 14 for details.

![Figure 4](image2.png) Comparison of the first four coefficients \(v_j(R)\) in the Legendre expansions of the CBS+corr potential and the SAPT potential.

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Legendre expansion of these potentials as functions of \( R \). The first three anisotropic terms with \( \lambda = 1, 2, 3 \) are even larger than the isotropic term with \( \lambda = 0 \); the term with \( \lambda = 2 \) is dominant. The coefficients of the SAPT potential are slightly smaller than those of the CBS+corr potential.\(^{10} \)

These potentials are also compared in Figure 5 in calculations of the differential cross sections from the initial state with \( j = 0 \) to the final states \( j' = 1, 4, 8, 12 \) calculated on the CBS+corr and SAPT potentials, at a collision energy of 513 cm\(^{-1} \). The similarity of the resulting DCSs illustrates that the already 18 year old SAPT potential is of nearly the same high quality as the more recent CBS+corr potential. The DCSs show the expected trend that the cross sections are largest for \( j' = 4 \) and that more backscattering occurs as the potential. The DCSs show the expected trend that the cross sections from the initial states with \( j = 0, 1, 2 \) to the final states at collision energy 513 cm\(^{-1} \). The fact that the cross sections are largest for \( \Delta j = 2 \) follows from the dominance of the term with \( \lambda = 2 \) in the Legendre expansion of the potential, Figure 4.

As mentioned in the Experimental section, the present experiment does not achieve pure initial-state selection. The parent CO beam contains a mixture of \( j = 0, 1, 2 \) and 2 states, which due to their different internal energy and quantum numbers show widely varying scattering behavior. This is illustrated in Figure 7, where DCSs are shown for the three initial states \( j = 0, 1, 2 \) excited to the same final state \( j' = 4 \). We took the population ratio of these states as 65:33:2\%, respectively. As expected, the initial-state averaged DCS (lower panel) is mainly determined by the 65\% \( j = 0 \) contribution but note that the scattering cross section increases with increasing \( j \) (decreasing \( \Delta j \)) and that the outer maximum in the DCS for \( j = 0 \rightarrow j' = 4 \) is much weaker for \( j = 1 \rightarrow j' = 4 \) excitation.

### 4.2. Vector Correlations.

Investigations of vector correlations in inelastic scattering processes reveal valuable information on the underlying dynamics.\(^{35} \) The angular momentum distributions in inelastic scattering are generally presented in terms of renormalized PDDCSs, but different expressions for these PDDCSs have been used in previous studies. Brouard et al.\(^{35} \) listed the relationship between the polarization moments and alignment parameters used in various papers. We present our alignment results in terms of the Hertel–Stoll renormalized \( A_{4}^{(j)}(\theta) \) polarization parameters, which are the irreducible components of the scattering density matrix related to the classical probability density function. They are defined in the scattering frame with the \( z \)-axis along the initial relative velocity vector \( \mathbf{k} \). \( A_{4}^{(j)}(\theta) \) is directly related to the conventional DCS, which reveals the vector pair correlation between the initial and final relative velocity vectors \( \mathbf{k} \) and \( \mathbf{k}' \), and \( \theta \) is the angle between \( \mathbf{k} \) and \( \mathbf{k}' \) in the collision plane, as shown in Figure 3. Polarization-dependent differential cross sections (PDDCSs), represented by the \( A_{4}^{(j)}(\theta), A_{12}^{(j)}(\theta) \), and \( A_{12}^{(j)}(\theta) \) polarization moments, describe the triple correlation between \( \mathbf{k}, \mathbf{k}' \), and the final rotational angular momentum \( j' \). In the case of inelastic atom–molecule scattering, the \( A_{4}^{(j)}(\theta) \) moment for the \( j', k \) correlation is related to the population of

![Figure 5. Comparison of state-to-state differential cross sections from \( j = 0 \) to \( j' = 1, 4, 8, 12 \) calculated on the CBS+corr and SAPT potentials, at a collision energy of 513 cm\(^{-1} \).](Image 104x303 to 256x661)

![Figure 6. Integral cross sections for elastic and inelastic scattering from the initial \( j = 0, 1, 2 \) states to the \( j' = 0–15 \) final states at collision energy 513 cm\(^{-1} \).](Image 324x567 to 564x749)

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Angular distributions extracted from velocity map images for collision-induced alignment from rotational energy-transfer processes can be expressed in the form

\[ I(\theta) = C \frac{d\sigma}{d\Omega}(\theta) [1 + \sum_{kq} A_{k}(\theta) F_{q}(\chi, \Theta, \phi)] \] (1)

where \( \frac{d\sigma}{d\Omega}(\theta) \) is the DCS, \( C \) is a constant factor that includes the effect of the density to flux correction, and the quantity in square brackets describes the renormalized alignment distribution. The function \( F_{q}(\chi, \Theta, \phi) \) contains all information on the experimental variables needed.\cite{14,35} In the case of \((2 + 1)\) REMPI detection, described first in this section, the experimental conditions are such that the \( F_{q}(\chi, \Theta, \phi) \) values in eq 1 are effectively zero (i.e., there is no alignment sensitivity in the experiment) and the DCS can be determined directly from the density-flux corrected image and compared with theory. Next, the angular distributions determined using polarization-sensitive \((1 + 1')\) REMPI detection are described.

4.3.1. Differential Cross Sections at 513 cm\(^{-1}\) Collision Energy Using \((2 + 1)\) REMPI Detection. Raw images taken at 513 cm\(^{-1}\) collision energy with \((2 + 1)\) REMPI detection are shown on the left-hand side of Figure 8 for final states in the range \( j' = 3 - 11 \). Simulated images from the IMSIMM program, which accounts for the divergence and velocity spread of the

![Figure 7. Comparison of state-to-state differential cross sections from \( j = 0, 1, \) and 2 to \( j = 4 \) at collision energy 513 cm\(^{-1}\).](Image 116x433 to 245x749)

![Figure 8. Raw experimental two-dimensional velocity map images of the \( j' = 3 - 11 \) final states using \((2 + 1)\) REMPI detection at collision energy 513 ± 40 cm\(^{-1}\), on the left-hand side. The direction of the initial relative velocity vector is shown as a white arrow in the image for the \( j' = 3 \) state. The color code is shown in Figure 1. Images simulated using the IMSIMM program are shown (middle column) for comparison with the experimental image. On the right-hand side experimental DCSs are compared with theoretical predictions for each final state, where the experimental curve is scaled by a constant factor to match theory.](Image 351x171 to 538x488)
molecular beams and their relative timing, as well as the laser ionization timing, volume, and propagation direction, are shown in the middle column. All final states from \( j' = 3 \) to 11 were measured except for \( j' = 5 \), in which case the S(5) and R(11) branches are fully overlapped. The S(6) transition is also overlapped with R(15), but the latter final state is very close to the energetic limit (Figure 1); its population is thus negligible.

As mentioned previously, detection with (2 + 1) REMPI under our experimental conditions showed no measurable sensitivity to the direction of the laser polarization. The experimental DCSs from the IMSIMM program are shown on the right-hand side of Figure 8 and compared with theoretical predictions.

Table 1. Frame Transformation Angles and \( F^{(k)}(\chi, \Theta, \phi) \) Factors

<table>
<thead>
<tr>
<th>( (\chi, \Theta, \phi) )</th>
<th>HIP</th>
<th>HOOP</th>
<th>VIP</th>
<th>VOOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\alpha, 2\pi/3, 0) )</td>
<td>0.625</td>
<td>0.625</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>( (\alpha/2, 2\pi/3, 0) )</td>
<td>0.375</td>
<td>-0.375</td>
<td>0.375</td>
<td>0.375</td>
</tr>
<tr>
<td>( (\pi/2, 2\pi/3, \pi/2) )</td>
<td>0.217</td>
<td>-0.217</td>
<td>-0.87</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Figure 9. Raw two-dimensional velocity map images of the \( j' = 5 \)–14 final states using \((1 + 1')\) REMPI detection at collision energy \( 840 \pm 40 \text{ cm}^{-1} \). The direction of the initial relative velocity vector is shown as a white arrow in the image for the \( j' = 5 \) state. The polarization of the (resonant) VUV photon is indicated by V for polarization perpendicular to the collision plane and H parallel to the collision plane. The sensitivity scale for each pair of images is adjusted to make the main features visible. The middle panel shows HIP, HOOP, VIP, and VOOP distributions extracted from these images and the right panel shows theoretical predictions corrected for the laser geometry. Each experimental curve was scaled by a constant factor to match the corresponding theory curve.

4.3.2. Polarization-Dependent Differential Cross Sections at 840 cm\(^{-1}\) Collision Energy. In previous work on collision-induced alignment in NO–Ar collisions, reasonable assumptions were made to extract the DCS and alignment functions from the data. The DCS was extracted from the image data \( I(\theta) \) by assuming the \( A_y^{(k)}(\theta) \) values from the
kinematic apse model or from a full quantum mechanical (QM) scattering calculation. For determining the \( A^2_0(\theta) \) values, the DCS was taken from the QM calculations. Note that three polarization parameters can be predicted from the kinematic apse model and all three are measurable. The \( A^2_0(\theta) \) parameter, however, is not accessible when \( k_{\text{aser}} \) is perpendicular to the initial velocity vector \( k \), as in the CO–Ar experiment described in ref 14. The frame transformation angles and functions \( F(F,\Theta,\phi) \) for the geometry in the present experiment are given in Table 1.

Following the procedures outlined in ref 14, the \( F(F,\Theta,\phi) \) factors are combined with the polarization moments to yield the angular distribution for each polarization geometry as

\[
I_{\text{HIP}}(\theta) = \frac{d\sigma}{d\Omega}(\theta)C[1 + 0.625A^2_0(\theta) + 0.375A^2_1(\theta) + 0.217A^2_2(\theta)]
\]

\[
I_{\text{HOOP}}(\theta) = \frac{d\sigma}{d\Omega}(\theta)C[1 - 0.5A^2_0(\theta) - 0.375A^2_1(\theta) - 0.217A^2_2(\theta)]
\]

\[
I_{\text{VIP}}(\theta) = \frac{d\sigma}{d\Omega}(\theta)C[1 - 0.5A^2_0(\theta) + 0.375A^2_1(\theta) + 0.217A^2_2(\theta)]
\]

\[
I_{\text{VOOP}}(\theta) = \frac{d\sigma}{d\Omega}(\theta)C[1 - 0.5A^2_0(\theta) + 0.375A^2_1(\theta) - 0.217A^2_2(\theta)]
\]

(2)

In the setup of ref 14 with \( \Theta = 90^\circ \) the HIP and HOOP distributions must be identical, so that the position and scaling of the rectangular region used to obtain the HOOP distribution could be adjusted to match the HIP distribution. The same position and scaling could then be used for the VOOP distribution. Here, we have \( \Theta = 120^\circ \) and it is apparent from the above equations that HIP and HOOP are not identical, so that this scaling method is not applicable. This problem is to measure also at a different \( k_{\text{aser}} \) direction; for example, at \( \Theta = 0^\circ \) where VIP = HOOP and HIP = VOOP. As this proved inconvenient, theory was again called on, and the relative cross sections from theory were used to calibrate the experimental scaling factor relating the HIP and HOOP curves. The same scaling was then applied to the experimental VIP and VOOP distributions. In this approach, the length of the integration region for HOOP and VOOP was fixed at the average radius of the annulus used for the HIP and VIP integrations.

Linear combination of the expressions in eq 2 yields the differential cross section

\[
\frac{d\sigma}{d\Omega}(\theta)C \approx \frac{1}{4}[I_{\text{HIP}}(\theta) + I_{\text{HOOP}}(\theta) + I_{\text{VIP}}(\theta) + I_{\text{VOOP}}(\theta)]
\]

\[
= \frac{d\sigma}{d\Omega}(\theta)C\left[1 + \frac{1}{16}A^2_0(\theta) + \frac{3}{16}A^2_1(\theta)\right]
\]

(3)

where, considering the small values of their scaling coefficients and their tendency to cancel each other, the last two terms in eq 3 are ignored. This approximation was confirmed to be valid by comparing the exact and approximate forms of eq 2 using the polarization moments and DCS from theory.

Other combinations yield the polarization parameters:

\[
A^2_0(\theta) = \frac{I_{\text{HIP}}(\theta) - I_{\text{HOOP}}(\theta)}{\frac{d\sigma}{d\Omega}(\theta)C} - 2
\]

\[
A^2_1(\theta) = \frac{I_{\text{HIP}}(\theta) - I_{\text{VIP}}(\theta)}{\frac{d\sigma}{d\Omega}(\theta)C} - 0.43A^2_2(\theta)
\]

\[
= \frac{I_{\text{HIP}}(\theta) + I_{\text{VIP}}(\theta)}{\frac{d\sigma}{d\Omega}(\theta)C} - 2 - 0.125A^2_0(\theta)
\]

\[
+ 0.653A^2_2(\theta)
\]

\[
A^2_2(\theta) = \frac{I_{\text{VOOP}}(\theta) - I_{\text{VIP}}(\theta)}{1.74\frac{d\sigma}{d\Omega}(\theta)C}
\]

(4)

where the two combinations for \( A^2_1(\theta) \) from the experimental data were averaged.

As shown in ref 14, \( (1 + 1') \) REMPI of CO allows measurement of polarization-dependent DCSs. Both V and H polarization images measured for \( j' = 5-14 \) final states using \( (1 + 1') \) REMPI detection on Q-branches around 154 nm are shown in Figure 9. In these measurements the collision energy is \( 840 \pm 40 \text{ cm}^{-1} \). For the \( j' = 5 \) state a CO-beam-only image was subtracted from the CO + He image, for higher \( j' \) states the parent beam signal is sufficiently far from the scattering ring.
that subtraction was not necessary. For \( j' < 5 \) no Q-branch probe transitions free of overlap with other states could be found. Raw H and V images (without density-flux correction) are shown in the left panel of Figure 9. HIP, HOOP, VIP, and VOOP angular distributions for each final state are shown in the middle panel of Figure 9. HIP and VIP curves are obtained by integration around the annulus shown schematically as circles superimposed on the \( j' = 9 \) V image, whereas the HOOP and VOOP curves are obtained from integration along the vertical stripes shown schematically on the \( j' = 9 \) H image.

As a test of the HIP−HOOP scaling procedure described above, the resulting HIP, HOOP, VIP, and VOOP curves (middle column) are compared with predictions from theory shown in the right column of Figure 9. In all cases scaling factors did not vary by more than a factor of 2 from the amplitudes of the raw data curves. Although the noise is considerable, the shapes and areas of each experimental curve are in reasonable agreement with theory for all measured final states. DCSs obtained by application of eq 3 are compared with theoretical predictions in Figure 10. Polarization moments extracted from the experimental I(θ) curves are shown in Figure 11.

4.4. Discussion. CO is a closed shell molecule with a relatively small dipole moment (0.122 D), and He is a small atom with a low polarizability. Therefore, the interaction of CO with He is dominated by short-range interactions that require small impact parameters. For this repulsive interaction system L-type rainbows, which have been shown to have remarkable polarization effects for NO−Kr collisions are not expected or seen in the theoretical analysis. Instead, the kinematic apse model, which describes the system classically as a hard sphere colliding with a rigid ellipsoid, should yield an accurate prediction of collision-induced alignment effects, as shown in previous studies of NO−He, −Ne, and −Ar collisions. Indeed, the polarization moments predicted by theory here for the CO−He system are almost quantitatively similar to those predicted for the NO−He, Ne, and Ar systems. The magnitude of the energy-transfer cross sections between CO−He and CO−Ar, however, is quite different. For example, the ICS for the \( j' = 7 \) ←\( j = 0 \) excitation for CO−Ar is 8 times larger than that for CO−He at 513 cm\(^{-1}\) collision energy, and similar differences are found for the NO−He versus NO−Ar systems. The smaller cross sections make collision-induced alignment studies with He as the collision partner much more difficult and up to the present only Meyer has reported CIA studies of NO−He at the (high) collision energy of 1185 cm\(^{-1}\). CO−He is thus not an easy system for experimental study, and as expected, this results in lower quality DCS and alignment data than CO−Ar.

Figure 11. Renormalized alignment moments for \( j' = 7−14 \) computed with the use of eq 4 from the HIP, HOOP, VIP, and VOOP angular distributions extracted from the measured images (red) in comparison with calculated moments (black) at collision energy 840 ± 40 cm\(^{-1}\).
Regardless of the small cross section, the DCSs recovered when \((2 + 1)\) REMPI detection is used (Figure 8) and agree quite well with theoretical predictions. Note again that theory takes into account the mixture of initial states in the experiment. With the relatively high-intensity laser pulses needed for the \((2 + 1)\) REMPI detection, it is clearly possible to detect a significant fraction of the scattered molecules without distortion due to complete saturation or space charge. In this aspect, the laser confocal diameter is roughly 30 μm for the 20 cm focal length lens used, but the ≈1 cm confocal length of the laser beam exceeds the length of the \(≈4 \times 4 \times 4\) mm collision volume.

DCSs recovered from the full polarization study using \(1 + 1’\) REMPI at 840 cm\(^{-1}\) collision energy are also in reasonable agreement with theory, although for the lower \(j’\) final states the second rainbow peak in the side to backscattering region is broader than predicted. The shape of the DCS, especially in this region, is sensitive to the value of the polar angle \(\Theta\) and to the amount of \(j = 0\) versus \(j = 1\) in the initial beam. Considering that the experimental \(I(\theta)\) curves match the shape of the corresponding theory curves (Figure 9), when only HIP and HOOP are scaled using theory, again confirms the general agreement of experiment and theory for the DCSs. Rescaling of the experimental curves was necessary because the total sensitivity for each image could not be held sufficiently constant when the laser polarization was rotated.

The direct extraction method yields polarization parameters (Figure 11) that are also qualitatively in agreement with theory predictions. As is typical, the \(A_{02}^{02}(\theta)\) parameter is most reliable whereas the \(A_{fi}^{j'j}(\theta)\) parameter (obtained only from the VIP-VOOP curves) is noisy and quite sensitive to the scaling method. The \(A_{fi}^{j'j}(\theta)\) parameters show the expected shapes in general, although for the weak and quite small \(j' > 10\) images substantial deviations are observed.

All three experimental polarization parameters tend to reach their minimum values, in contrast to previous work on NO–rare gas studies, where typically \(A_{fi}^{j'j}(\theta)\) reached only \(-0.4\) to \(+0.5\) instead of \(-1.0\) at the backscattering angle. This difference could be due to the lack of nuclear spin in CO compared to NO, where any stray magnetic field could depolarize the nascent NO on the time scale of the scattering measurement. Another effect, as suggested by Brouard and co-workers, is depolarization due to secondary collisions. In our measurement, both the DCSs and polarization parameters show significant deviation from theory in the most forward scattering direction. We believe this is due mainly to elastic scattering following the inelastic event, as discussed next.

For any study of inelastic (or reactive) scattering the effects of elastic scattering must be considered. Two features of elastic scattering are a much larger total cross section and strongly forward scattering. Figure 12 shows the elastic scattering DCS for the \(j' = 7\) state, a typical final product measured in this study. To visualize both the magnitude of the cross section and the angular distribution, the DCS is weighted by \(\sin \theta\) in Figure 12 where the area under the curve is then the integral cross section. The \(j = 7\)–7 ICS (similar to all of the other elastic ICSs) is 37 times larger than the \(j = 0\)–7 ICS, which is typical for all of the lower initial states, as seen in Figure 6. The probability for an elastic collision after the \(j' = 7\) state is formed but before laser ionization takes place under the present condition of \(≈5\%\) inelastic scattering is close to 100%. Also apparent in Figure 12 is that although the elastic scattering is mostly forward, even at 20° there can be a significant effect on collisions. In the forward scattering region, elastic scattering can thus cause significant depolarization, and forward scattering is where the largest deviation in the polarization parameters between experiment and theory is seen in Figure 11. Elastic scattering will not cause significant deflection of the nascent molecules. Once inelastically scattered, however, these molecules are no longer moving with their parent beam velocity and further collisional depolarization and elastic scattering with the carrier gas of the parent beam with much higher cross sections becomes possible.

For the present CO–He system, collisional depolarization appears to mainly affect the forward scattering region whereas the backscattering region shows the maximum possible collision-induced alignment, within the large error margin of the experiment. For the CO–Ar system where the inelastic scattering cross section is nearly an order of magnitude larger, collisional depolarization should play a more important role and this is indeed observed in the preliminary results of ref 14, where in the backscattering region the polarization parameters do not reach their maximum expected values. Finally, for very dilute systems such as those with hexapole or Stark deceleration state selection the probability of an inelastic collision can be
sufficiently low that depolarization by elastic scattering with the rare gas partner should not be important.

5. CONCLUSION

The rotational excitation of CO molecules due to scattering with He atoms at collision energies of 513 and 840 cm$^{-1}$ was studied in a crossed molecular beam setup and velocity map imaging (VMI) with state-selective and polarization-sensitive detection through (1 + 1)’ and (2 + 1) REMPI. The incoming CO beam had a rotational temperature of $T_{rot} \approx 3$ K with $j = 0$, 1, and 2 states populated in a ratio of 65:33:2%. Differential cross sections (DCSs) and alignment parameters for a range of final $j$ values of CO were extracted from the measured images by a direct analysis procedure described by Suits et al., but generalized here to account for a different laser beam direction. The same DCSs and alignment parameters, averaged over the initial-state distribution of CO, were obtained from quantum mechanical close-coupling calculations based on two accurate $ab$ initio potentials for CO–He. Good agreement between the experimental and theoretical results was found, in general, which illustrates the reliability of the experiment, as well as of the procedure used to extract state-to-state differential and polarization-dependent differential cross sections from the measured images.

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Notes
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