Observation of anisotropic interactions and molecular orbitals of CO upon collision with He\(^*(2\,^3S)\) atoms by two-dimensional Penning ionization electron spectroscopy

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Abstract. By collision-energy/electron-energy-resolved 2D Penning ionization electron spectroscopy as well as by theoretical calculations of the collisional ionization dynamics, the outer shape of molecular orbitals for ionization to X(\(^2\Sigma^+\)) and A(\(^2\Pi\)) states of CO\(^+\) was sensitively probed, and the anisotropy of the interaction between He\(^*(2\,^3S)\) and CO was determined. Ionization to the B(\(^2\Sigma^+\)) state of CO\(^+\) was assigned to autoionization from superexcited states by angle-resolved electron spectroscopy and theoretical simulations.

1. Introduction

In the collision of a molecule M with an excited helium atom He\(^*\), having excitation energy larger than the ionization potential (IP) of the molecule M, a chemi-ionization process known as Penning ionization (He\(^*\) + M \rightarrow He + M\(^+\) + e\(^-\)) can occur [1]. Unlike other experimental methods, using photons or electrons, the collisional ionization of molecules by collision with excited atom beams in a metastable state is an excellent technique to probe the outer electrons of molecules (electrons in the region far from the nuclei). Since many chemical and physical phenomena that originate from interactions between molecules depend on the outer region of the molecules, the spatial extent of molecular orbitals (MOs) is of great importance. For example, the collisional ionization of N\(_2\) with He\(^*(2\,^3S)\) metastable atoms was used to determine the outer MOs of N\(_2\) [2].
The analysis of the kinetic energy of electrons ejected due to the collisional ionization process with metastable atoms [3] is called Penning ionization electron spectroscopy (PIES) [4]. With regard to the branching ratios in PIES, ionization probabilities are shown to be strongly governed by the overlap between the He 1s orbital and the MO to be ionized, and they are related to the electron density of the MOs outside the repulsive surface of a target molecule [5]. The interaction potential energy surface, $V^*$, between He* and M represents the target “molecular surface”, which we define as the minimum distance between He* and the nuclei of M as a function of the collision energy ($E_c$). The change of the target molecular surface with $E_c$ leads to a change in the effective overlap between the He 1s orbital and the target MOs. Since the electron distribution in the individual MOs is spatially localized, the ionic-state-resolved measurement of the Collision Energy Dependence of the Partial Ionization Cross Section (CEDPICS) provide important information on the anisotropy of He molecular surface [6] of the entrance channel of Penning ionization without any controlling of the alignment of the target molecule. We use two-Dimensional Penning Ionization Electron Spectroscopy (2D-PIES) to study CEDPICS as a function of the electron kinetic energy $E_e$ [7,8].

The angular distributions of the outgoing electrons in the exit channel of Penning ionization is well studied [9-13]. Ebbing and Niehaus measured the angular distributions of Penning electrons for several targets with He* atoms as a function of the angle $\theta$ with respect to the incoming He* beam vector [10]. They observed that the angular distributions for ionization by He*(2$^3$S) are strongly anisotropic and asymmetric in the case of a “hard-sphere” collision. This feature was explained as evidence for the applicability of the electron exchange model, in which an electron of a MO of M is transferred to the inner vacant orbital of an excited atom A*, and simultaneously an excited electron A* is ejected, thereby causing the internal distributions of outgoing electrons to be anisotropic [9]. Niehaus calculated the internal angular distribution of the outgoing electrons for ionization of Ar with He* [3]. In some other studies [11-14], the isotropic angular distributions of electrons via auto-ionization processes of target molecules by excitation transfer from A* to M have been observed despite the repulsive interactions between A* and M.

Here, we have investigated the Penning ionization process of CO in collisions with He*(2$^3$S) by 2D-PIES, as well as by angle-resolved PIES techniques, to determine anisotropic interactions between He*(2$^3$S) and CO, as well as the wave functions for the entrance (molecular orbitals) and exit (electron ejection) channels of the collisional ionization by theoretical calculations.

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2. Experimental

A metastable beam of He\(^*\)(2\(^1\)S, 2\(^3\)S) atoms was produced by a nozzle discharge source with a hollow tantalum cathode [6]. Then the metastable beam was pulsed by a mechanical chopper with four slits rotating at ca. 350 Hz, and was irradiated by the light from a water-cooled spirally-shaped helium gas discharge lamp in order to quench the He\(^*\)(2\(^1\)S) component [6]. Liquid nitrogen cooling of the metastable beam source was used for the low collision energy region around 20-80 meV [15]. Magnetic bottle effect by a strong-field permanent magnet (ca. 0.08 T) and a weak-field by guiding solenoid (ca. 0.0006 T) around the electron flight tube were utilized for a 4\(\pi\) electron correction. The electron energy spectra were obtained by integrating electron signals with the retarding type electron analyzer at the measurement of 2D-PIES [16].

For the measurement of the angular distribution of Penning electrons, a collision cell fixed to a turntable with a hemispherical electrostatic analyzer was rotated through the angle \(\theta\) (from 40\(^\circ\) to 140\(^\circ\)) between the initial He\(^*\) atomic beam vector and the electron detection direction [17].

![Diagram](image_url)

**Figure 1.** The intermolecular axis vector \(\mathbf{R}\) is directed from the center of mass of the target molecule toward a He\(^*\) atom. Angles are defined as \(\omega\) (between the molecular axis and the vector \(\mathbf{R}\)), \(\gamma\) (between the vector \(\mathbf{R}\) and the electron ejection direction), and \(\theta\) (between the electron ejection direction and the He\(^*\) beam).
3. Calculations

Miller et al. [18] derived the ionization width, $\Gamma$, by considering an electron ejection direction $\gamma$ at the distance $R$ between a He$^+$ atom and the center of mass of the target molecule, as well as the angle $\omega$ between the vector $\mathbf{R}$ directed from the center of mass of the target molecule towards a He$^+$ atom and the molecular axis (Fig. 1):

$$\Gamma(R, \omega, \gamma) = 2\pi \rho |\Psi| H - E |\Psi'|^2 = 2\pi \rho \left| \sum_{lm} Y_{lm}(\gamma) i^{-l} \exp(i\sigma_l) I_{lm} \right|^2, \quad (1)$$

where $\Psi$ denotes the wave function for the initial state, $\Phi$ the wave function for the final state, $\rho$ the density of the final states. $Y_{lm}(x)$ are the spherical harmonics for electron ejection around the center of the He atom, with angular momentum $l$ and projection quantum number $m$. $\sigma$ is the phase shift and $I_{lm}$ the matrix element of the transition. In the present study, the ionization width for the $j$-th ionic state of the molecular targets was approximated to be

$$\Gamma_j \approx \sum_{lm} Y_{lm}(\gamma) i^{-l} \exp(i\sigma_{l,j}) \left| \langle \phi_{lm,j} | \Psi_{1s} \rangle \right|^2 \left| \langle \Psi_{1s} | \phi_j \rangle \right|^2, \quad (2)$$

where $\phi$ denotes the ionized orbital, $\Psi_{1s}$ ($\Psi_{2s}$) the 1s (2s) orbital of the He atom, and $\phi_{lm,j}$ the continuum orbital. Since $\Psi_{2s}$ and $\phi_{lm,j}$ are significantly more diffuse functions than $\phi$ and $\Psi_{1s}$, and their variation of $\langle \phi_{lm,j} | \Psi_{2s} \rangle$ with $\mathbf{R}$ is negligible as compared to that of $\langle \Psi_{1s} | \phi_j \rangle$, the amplitude of the last part ($\langle \phi_{lm,j} | \Psi_{2s} \rangle$) of the equation vanishes except for $\sigma$ symmetric partial waves ($m = 0$) and is assumed to be independent of $\mathbf{R}$ [19].

For theoretical CEDPICS, the transition probability $T_j$ of each trajectory step is calculated by the following equations:

$$T_j(t)dt = S(t) \frac{K_j \left| \langle \Psi_{1s} | \phi_j \rangle \right|^2}{\eta} dt,$$

$$S(t) = 1 - \sum_j T_j^{int}(t), \quad (3)$$

where $S(t)$ denotes the survival probability of He$^+(2^3S)$ at a certain time $t$, $T_j^{int}$ is the integrated partial transition probability, and $K_j$ is the ionization parameter. Classical trajectory calculations of He$^+$ atoms were performed on a modified potential energy surface from Li($2^2S$) model calculations, which use a Li atom instead of a He$^+(2^3S)$ atom based on the similarity in
Figure 2. (a) Contour maps of the potential energy surface for CO with a He\(^*\)(2\(^3\)S) atom (V\(^*\)) and a Li\(^2\)S) atom (V\(_0\)) with an energy spacing of 50 meV in 0-800 meV. (b) Collision energy dependence of total (filled circle) and partial Penning ionization cross sections (CEDPICS) for CO/He\(^*\)(2\(^3\)S). Simulated CEDPICSs by using optimized MO (CEDPICS-MO) and SCF-MO with the minimal basis set (SCF/Min) are drawn with solid and broken lines, respectively. Absolute value of ionization cross section was obtained by Parr et al. [21] (double circle).
interaction with target atoms [3]. In each of the trajectory calculations, the orientation of a molecule and the impact parameter $b$ were set randomly, and finally partial ionization cross sections $\sigma_j (\equiv \int 2\pi b T_j(t)dt db)$ were calculated. Here by optimization of parameters in the CEDPICSs simulation [2,20] with a nonlinear least square fitting method, the difference between the interactions of He*-M ($V^*$) and Li-M ($V_0$) was improved and the ionization parameter $K_j$ in eq. (3) was determined.

4. Results and Discussion

Figure 2(a) and (b) show the interaction potential contour maps ($V_0$ and $V^*$) and CEDPICS of CO in collision with He*(2\(^3\)S) atoms, respectively. The total ionization cross section of CO/He*(2\(^3\)S) was measured by the detection of produced ions [21]. Simulated CEDPICSs using classical trajectory calculations are drawn with two types of lines in Fig. 2(b). The three ionic states $X(2\Sigma^+)$, $A(2\Pi)$ and $B(2\Sigma^+)$, correspond to the electron ejection from the outer region of 5$\sigma$, 1$\pi$, and 4$\sigma$ MOs of CO, respectively. The ionization cross section for the $A2\Pi$ state increases most steeply with the increase in $E_c$, while the increase of the ionization cross section for $X2\Sigma^+$ state is saturated. The different slopes of CEDPICS reflect the highly anisotropic interaction potential around CO; the steepness of the repulsive interaction $V^*$ is larger for the ionization region around the C atom ($X2\Sigma^+$) rather than for the off axis directions around the O atom ($A2\Pi$).

a. Ab initio and optimized molecular orbitals

As an initial guess for the MO functions ($\phi_j$) used for optimizing to the observed CEDPICSs, SCF MOs with the minimal basis set (STO-6G) were used (SCF-Min, broken lines) with the $V_0$ interaction potential. The optimization was performed for theoretical CEDPICSs under a double-$\zeta$ framework with variable coefficients, and the basis set exponents of 16 contracted Gaussian type orbitals (CGTO) (CEDPICS-MO, solid lines) were simultaneously determined with the $V^*$ potential [2]. The results of SCF-Min in Figure 2(b) overestimate the steepness of the CEDPICS. Since electron densities of SCF-Min are mainly concentrated around the center of CO, the magnitude of the overlap integral in eq. (4) increases rapidly at the collision of He* atoms with CO. The calculated CEDPICSs in the whole $E_c$ range were shown to be dramatically improved by modifying the shape of MOs and $V^*$ as indicated by the solid lines.
Figure 3. (a) Electron density contour maps for various MOs corresponding to the observed three ionic states of CO. (b) Electron density plots of various kinds of MOs as a function of distance $r$ from the center of mass of the target molecule. Optimized MO (CEDPICS-MO) is plotted with open circle, and theoretical MOs, Hartree-Fock (HF: solid line), Kohn-Sham (KS: broken line), SCF with the minimal basis (dotted line), and Dyson orbitals with 6-311+G* basis.
sets (chained line), are also shown.

In order to compare CEDPICS-MOs with theoretical MOs, the electron density maps and the electron density \( \rho_e(r) \) of the individual MO, plotted as a function of distance \( r \) from the center of mass of CO, are shown in Figure 3 (a) and (b), respectively. Hartree-Fock (HF) and Kohn-Sham (KS) MOs with the standard B3LYP functional [22] were obtained in SCF calculations by using a large basis set composed of 138 ([7s6p4d2f]) CGTO at near Hartree-Fock limit [2]. The electron density of SCF-Min decreases more rapidly with the distance \( r \) than those of other MOs. Different from the SCF-Min MOs, CEDPICS-MOs are comparable to HF or KS MOs except for the \( \text{B}^2\Sigma^+ \) state, and it should be noted that KS orbitals extend outside further than HF orbitals, whereas CEDPICS-MOs are more compact than HF, as with the case for N\(_2\) [2].

The shape of CEDPICS-MO for the \( \text{B}^2\Sigma^+ \) state obtained here is quite different from HF and KS orbitals. In order to examine the electron correlation and orbital relaxation effects in ionization events, we have calculated Dyson orbitals \( \equiv \langle \Psi_N^0 | \Psi_{j}^{N-1} \rangle \) which are defined as the overlap between the wave functions of the N-electron neutral ground state and the \( j \)-th ionic state by the cluster expansion configuration interaction (CI) method [23] with 6-311+G* basis functions (Fig. 3(b)). The Dyson orbitals with 6-311+G* basis functions gave the smallest error in ionization potential (IP) energy values (ca. 0.12 eV) compared with experimental IPs among several basis functions we tried. In spite of the surprising agreement of CEDPICS-MOs and Dyson orbitals for \( \text{X}^2\Sigma^+ \) and \( \text{A}^2\Pi \) states, the electron density of the calculated Dyson orbital for \( \text{B}^2\Sigma^+ \) state decreases more rapidly than those of HF and KS 4\( \sigma \) orbitals around the O atom. Although we can conclude that the electron correlation and orbital relaxation effects are not small in ionization to the \( \text{B}^2\Sigma^+ \) state of \( \text{CO}^+ \), the disagreement between CEDPICS-MO and Dyson orbital for \( \text{B}^2\Sigma^+ \) state should be noted. In a next step, it was necessary to examine the ionization mechanism for the \( \text{B}^2\Sigma^+ \) state by observation of the ejected electron angular distributions for \( \text{CO-He}^+(2^3\text{S}) \) collisional ionization.

b. Angular distribution of Penning electrons

Figure 4(a) shows the laboratory angular distributions of the ejected electrons in the Penning ionization of \( \text{CO-He}^+(2^3\text{S}) \) at \( E_c \) of 100 and 200 meV. Two ionic states (\( \text{X}^2\Sigma^+ \) and \( \text{A}^2\Pi \)) showed asymmetric angular distributions with respect to \( \theta = 90^\circ \), while the angular distribution for \( \text{B}^2\Sigma^+ \) state is considerably different and it has a maximum below \( \theta = 90^\circ \). The feature for \( \text{X} \) and \( \text{A} \) states indicates that the interaction potential of the \( \text{CO-He}^+(2^3\text{S}) \) system has a negligible
potential well, and the ejection direction of electrons strongly depends on the orientation of the target molecule and the excited atom during ionization [9,10,16].

![Figure 4](image-url)

**Figure 4.** (a) Angular distributions of Penning electrons for the CO-He$^+$ system at the collision energy of 100 meV and 200 meV. Symbols and curves represent experimental and calculated angular distributions of Penning electrons, respectively. (b) Polar diagram of the molecular frame electron angular distribution $F_j(\gamma)$ of each ionic state for the CO-He$^+$ system for $E_c$ of 100 meV (solid line) and 200 meV (dotted line).
We have analyzed the laboratory angular distributions of the ejected electrons for CO-He*\(^{2}S\) by theoretical calculations as shown in Fig. 4(a). In accordance with the methods adopted by Ebing and Niehaus for the angular distribution of Penning electrons [10], we have used partial waves \(l = 0, 1\) with a Legendre function, a phase shift \(\delta_l = \sigma_{l,j} - \sigma_{0,j} - (\pi/2)\) and the relative modulus of the ratio of amplitudes for s-waves and p-waves (\(\xi_j\)) in the calculation of ionization width, via:

\[
\Gamma_j(R, \omega, \gamma) = F_j(\gamma)G_j(R, \omega) = \left| \exp(i\sigma_{0,j})p_{0,j} + i^{-1}\exp(i\sigma_{1,j})p_{1,j} \cos \gamma \right|^2 G_j(R, \omega) \\
= \alpha_j(1 + 2\xi_j^2) \cos \delta_j \cos \gamma + \xi_j^2 \cos^2 \gamma G_j(R, \omega),
\]

where \(F_j(\gamma)\) denotes internal angular distributions in molecular coordinate at the center of a He* atom, \(G_j(R, \omega)\) is \(K\left| \left\langle \Psi_{2s_{j}} | \phi \right\rangle \right|^2\) in eq. (3), \(p_{l,j}\) the overlap integral \(\left\langle \phi_{l,j} | \Psi_{2s_{j}} \right\rangle\), and \(\alpha_j\) is a normalizing coefficient. The phase shift \(\delta_j\) and relative modulus \(\xi_j = (p_{1,j} / p_{0,j})\) were assumed to be independent of \(R\) and \(\omega\). The angle between the electron ejection direction and the He* beam can be defined as \(\theta\) (Fig. 1). We calculated ejected electron distributions \(I_j(\theta)\) for three ionic states at randomly generated molecular orientations and \(\omega\) values by the classical trajectory calculations with \(V^*\) and SCF-MOs (6-311+G*) at \(E_c\) of 100 and 200 meV. Then we optimized these two parameters (\(\delta_j\) and \(\xi_j\)) for \(F_j(\gamma)\) to reproduce the observed \(\theta\) dependence of the electron ejection (Fig. 4(a)).

Figure 4(b) shows the molecular frame electron angular distribution of each ionic state \(F_j(\gamma)\). The distribution of \(F_j(\gamma)\) is shifted towards the helium atom for the \(X^2\Sigma^+\) and \(A^2\Pi\) states similar to the cases with Ar atoms [3] and \(N_2\) [16], while the electron angular distribution for \(B^2\Sigma^+\) state is shifted towards the CO molecule. In addition, the optimized CEDPICS-MO for the \(B^2\Sigma^+\) state in Fig. 3(a) showed small electron density distribution around the O atom. These results may reflect a different ionization mechanism for the \(B^2\Sigma^+\) state from that of the \(X^2\Sigma^+\) and \(A^2\Pi\) states by the normal electron exchange type Penning ionization process. In the ionization process related to the \(B^2\Sigma^+\) state, it is interesting that the electron transition is not localized around the O atom and that the electron ejection occurs on the opposite sides of the He atom in the CO-He colliding system.
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