Nonresonant two-photon mass analyzed threshold ionization and zero kinetic energy photoelectron investigation of the $\tilde{X}^2B_1$ ground state of CH$_2$CO$^+$ and CD$_2$CO$^+$

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Rotationally resolved nonresonant two-photon mass analyzed threshold ionization (MATI) and zero kinetic energy (ZEKE) photoelectron spectra of CH$_2$CO$^+$ and CD$_2$CO$^+$ are reported. The spectra are dominated by the origin band and totally symmetric $a_1$ vibrations, $v_4$ (C=C symmetric stretch) and $v_2$ (C=O asymmetric stretch) for CH$_2$CO$^+$, and $v_1$ (C=O asymmetric stretch), $v_5$ (C=C symmetric stretch), and $v_2$ (CD$_2$ scissor) for CD$_2$CO$^+$. In addition, several weaker bands are observed in the MATI spectra: $v_1$ (CH$_2$ scissor) in CH$_2$CO$^+$; $b_1$ vibrations $v_3$ and $v_6$ (C=C=O linear bend and CH$_2$ wag) in both isotopomers; $b_2$ vibration $v_8$ (CD$_2$ rock) for CD$_2$CO$^+$; $b_2$ vibration $v_9$ (C=C=O linear bend) for CH$_2$CO$^+$; as well as overtones and combination bands. Rotational structure of the origin band is dominated by three very strong $\Delta K_a = \pm 1$ bands with 2 orders of magnitude weaker $\Delta K_a = \pm 3$ bands. A similar $\Delta K_a = \pm 1$ three-band pattern is observed for the $a_1$ vibrational modes. For the $b_1$ modes a single-band pattern resulting from the $\Delta K_a = 0$ selection rule is present. Fundamental wave numbers for six vibrational modes of CH$_2$CO$^+$ and seven modes of CD$_2$CO$^+$ are determined. Rotational analysis of the partially resolved ZEKE spectra yields the ionization potentials (77539.4$\pm$2.0 cm$^{-1}$ for CH$_2$CO and 77534.3$\pm$2.0 cm$^{-1}$ for CD$_2$CO) and rotational constants for the ground states of both ketene cations. © 2002 American Institute of Physics [DOI: 10.1063/1.1506157]

I. INTRODUCTION

Spectroscopy and photochemistry of ketene, CH$_2$CO, has been extensively studied in the past. Electronic states of this 16-valence–electron molecule have been investigated by ultraviolet absorption,\textsuperscript{1–4} vacuum-ultraviolet absorption,\textsuperscript{5} and resonance-enhanced multiphoton ionization\textsuperscript{6} spectroscopic techniques as well as studied theoretically.\textsuperscript{7,8} The lowest ionization potential (IP) of CH$_2$CO was first estimated by Price \textit{et al.}\textsuperscript{5} from Rydberg series extrapolation at 77429 cm$^{-1}$. Later, Ashfold \textit{et al.}\textsuperscript{6} determined the first IP to be equal to 77497$\pm$10 cm$^{-1}$ from the onset of three-photon ionization. As a good prototype of an asymmetric top molecule, ketene has also received considerable attention from vibrational and rovibrational spectroscopists. Accurate rotational constants for the ground state of ketene and its deuterated isotopomer (CD$_2$CO) have been obtained from microwave and millimeter-wave spectra.\textsuperscript{9–11} The nine vibrational normal modes have also been extensively studied by infrared spectroscopy.\textsuperscript{12–21} Interest in photochemistry of ketene has been primarily motivated by the two following reasons. On the one hand, ketene is a convenient photochemical source of both the singlet and the triplet methylene radical (CH$_2$)\textsuperscript{2,23} which is an extremely interesting and important system for spectroscopy, chemistry, and electrochemistry. On the other hand, photodissociation of ketene provides an important test case for investigation of kinetics and dynamics of unimolecular decomposition.\textsuperscript{24–27}

Unlike the neutral molecule, the ketene cation has not been studied much. Photoelectron spectra of CH$_2$CO$^+$ and CD$_2$CO$^+$ have been reported by several research groups.\textsuperscript{28–31} In these studies, adiabatic ionization energies corresponding to the ground electronic state as well as to five excited electronic states of the CH$_2$CO$^+$ and CD$_2$CO$^+$ cations were determined. Vibrational progressions were analyzed and frequencies of three totally symmetric modes were obtained. Due to a rather poor resolution associated with the traditional photoelectron spectroscopy, none of the vibrational features showed resolved rotational structure.

Very recently Willitsch \textit{et al.}\textsuperscript{32} have observed rotationally resolved zero kinetic energy (ZEKE) photoelectron spectra of CH$_2$CO$^+$ and CD$_2$CO$^+$ in their ground electronic state using vacuum ultraviolet (VUV) single photon excitation. They determined accurate IP [IP(CH$_2$CO) = 77538.7(7) and IP(CD$_2$CO) = 77533.4(7) cm$^{-1}$], wave numbers of three $a_1$
The $\tilde{X}^2 B_1$ state of $\text{CH}_2\text{CO}^+$ range is estimated to be significantly smaller ($\sim 0.5 \text{ cm}^{-1}$). Typical UV beam output energies were equal to 1.5 mJ/pulse.

Ketene and deuterated ketene were prepared by pyrolysis of acetic anhydride and $d_2$-acetic anhydride$^{36}$ flowing through a pyrex tube heated to 850 K. Unreacted acetic anhydride and other less volatile products of the pyrolysis were trapped in a cold finger trap immersed in a dry ice–acetone bath. Ketene was collected in a liquid nitrogen trap downstream, vacuum distilled twice between 195 and 77 K, and stored in the dark at liquid nitrogen temperatures for further use.

For our experiment, a ketene/He mixture was prepared in a stainless steel reservoir. The reservoir was filled with ketene up to a pressure of 500 Torr (66.7 kPa) at room temperature and diluted by ultrahigh purity helium to a total pressure of 56 psi (386 kPa). The ketene/He mixture was subsequently introduced into the source chamber in a supersonic jet expansion through a nozzle (250 $\mu$m diameter) of a pulsed piezoelectric valve operating at a repetition rate of 10 Hz. The molecular beam was formed by skimming the supersonic jet with a conical skimmer (1.5 mm diameter, 5 cm from the nozzle) and introduced into the ionization chamber. The master trigger pulse triggered three digital delay generators (Stanford Research Systems, DG 535), which synchronized the valve opening, laser firing, dye laser scanning, and pulsing of various voltages to $E_2$, $E_3$, and $E_4$ grids.

The ionization chamber was pumped by two turbomolecular pumps with a pumping speed of 500 l/s each. The source chamber was pumped by two other turbomolecular pumps with a pumping speed of 2000 l/s each. Under operating conditions, the source chamber and the ionization chamber were maintained at typical pressures of $5 \times 10^{-6}$ Torr (670 $\mu$Pa) and $5.4 \times 10^{-6}$ Torr (7.2 $\mu$Pa), respectively.

The time-of-flight (TOF) mass spectrometer, consisting of ion optics, a field-free drift tube, and a three-stage microchannel plate detector, was shielded from external magnetic fields by a single layer of 1 mm thick $\mu$-metal. The ion optics was composed of four parallel copper mesh grids, labeled from the bottom to the top as $E_1$, $E_2$, $E_3$, and $E_4$. The $E_2$ and $E_3$ grids were separated by 3 cm. The molecular and the laser beams intersected at right angles midway between these two grids. The electrons or the ions, generated by either photoionization or pulsed field ionization, were extracted by the electric field between the $E_2$ and $E_3$ grids, accelerated, and drifted along the field free flight tube towards the detector.

Both ZEKE and MATI detection schemes were used in this work. Both techniques rely on delayed pulsed field ionization of highly excited long-lived Rydberg states, located just a few cm$^{-1}$ below an eigenstate of the molecular cation. In the ZEKE detection scheme used in this experiment, the pulsed electric fields were arranged as follows. The first pulse of 433 mV/cm (duration = 1.7 $\mu$s) was created between the $E_2$ and $E_3$ electrodes by applying a negative voltage to the $E_3$ grid after a delay time of 130 ns with respect to the firing of the excitation laser. This pulse was designed to remove prompt electrons arising from the direct photoionization of the ketene molecule. Therefore, it was called a dis-
crimation pulse. The second field pulse (ionization pulse) of 400 mV/cm (duration = 5 μs) was created between the E2 and E3 electrodes by applying a negative voltage to the E2 grid 1.8 μs after the laser excitation in order to field ionize the long lived Rydberg states and to extract the ZEKE electrons. The third electric field pulse between E1 and E4 (acceleration pulse) with a duration of 20 ns and an amplitude of 22 V/cm generated by applying a short positive voltage pulse to the E4 grid 45 ns after the start of the ionization pulse was used to accelerate the ZEKE electrons toward the detector. The short pulse was obtained by passing a step voltage pulse (Stanford Research Systems, DG 535) through a capacitor. In the ZEKE experiment, the E1 grid was grounded. The above described ZEKE detection scheme resulted in full width at half maximum of the narrowest lines in the range 0.8–1.0 cm⁻¹, most of which was attributed to the laser bandwidth.

Two schemes were used to detect ketene cations created in the MATI experiments. In both schemes, the E1 and E4 grids were grounded, while various voltages were applied to E2 and E3. In the first MATI scheme, hereafter labeled as MATI scheme A, the E2 and E3 grids were grounded during the laser excitation of high-n* Rydberg states. The first (discrimination) pulsed electric field of 1 V/cm amplitude and 1.81 μs duration was created by applying a low negative voltage to the E3 grid 90 ns after the laser excitation. The second (delayed ionization and extraction) pulsed field of 733 V/cm was triggered 230 ns after the end of the first pulse by applying a high positive voltage to the E2 grid. Prompt ions were attracted to E3 by the first pulsed field, thus separated from the highly excited neutral ketene molecules remaining at the center. On application of the second pulse, the MATI ions produced by delayed pulsed field ionization gained more kinetic energy, thus higher drift velocity, than the prompt ions and, therefore, arrived at the detector earlier. By gating the signal on the MATI ion group, the MATI scheme A spectrum was obtained.

In the second MATI scheme, hereafter labeled as MATI scheme B, a constant electric field of 1.04 V/cm (offset field) was applied between E2 and E3. It was used as the discrimination field to push the prompt ions toward E3. A 1.21 μs long voltage pulse applied to E3 400 ns after the laser pulse created a weak field of 1 V/cm, which field ionized high-n* Rydberg states in a very narrow range close to an ionization threshold. The resultant high resolution (HR) MATI ions drifted away from the center. A high voltage pulse on E2 triggered 2.62 μs after the end of the pulse on E3 created an additional electric field of 733 V/cm, which field ionized more high-n* Rydberg states, yielding low resolution (LR) MATI ions, and which accelerated the prompt, LR MATI, and HR MATI ions towards the detector. The three groups of ions arrived at the detector at different times, as shown in Fig. 4, and were monitored separately. The MATI scheme B is similar to that previously described by Dessent et al.37 The main difference is that we have used a constant offset electric field rather than a pulsed field as in the work of Dessent et al. Application of the constant offset field has simplified the experiment by reducing the number of pulse generators required.

Pulsed small-amplitude voltages (<40 V) in the ZEKE and MATI schemes were produced by a digital delay generator (Stanford Research Systems, DG 535). The high voltage pulse of 2200 V was generated by a high voltage pulser (Directed Energy, GRX-3.0 K-H) powered by a high voltage supply (Stanford Research Systems, PS 350). The ion or electron signals from the Z-stack MCP detector (Burle Electro-optics) were amplified by a fast preamplifier (Stanford Research Systems, SR 445), gated and integrated by a boxcar (Stanford Research Systems, SR 250), digitized using an analog to digital converter (National Instruments), and stored in a computer. The experiment was controlled using a home-written program.

III. BACKGROUND

The principle of both ZEKE and MATI techniques used in this project is based on excitation of high-n* Rydberg states very close to an ionization limit. In our experiments, the highly excited Rydberg states were populated in a nonresonant two-photon excitation. The nonresonant two-photon electric dipole excitation of a molecule is governed by the following rigorous selection rule:38

\[ \Gamma^\prime \otimes \Gamma^n \supseteq [\Gamma^\prime]^2 \equiv \Gamma^{(s)}, \]

where \( \Gamma^{(s)} \) describes transformation properties of the total internal wave function, while \( \Gamma^\prime \) and \( \Gamma^n \) are antisymmetric and totally symmetric representations of a molecular symmetry group appropriate for a given molecule. Substituting

\[ \Gamma^\prime \otimes \Gamma^n \supseteq \Gamma^{(s)}, \]

If the Rydberg electron is asymptotically decoupled from the molecular-ion core, which is a valid approximation for very highly excited Rydberg states, we can substitute in Eq. (1) and assuming that both the nuclear spin and the electron spin are decoupled from other angular momenta we get

\[ \Gamma^\prime \otimes \Gamma^{(s)} \supseteq \Gamma^{(s)} . \]

Assuming separability of the rotational, vibrational, and electronic wave functions we can write

\[ \Gamma^{(s)} = \Gamma_{\text{rot}} \otimes \Gamma_{\text{vib}} \otimes \Gamma_{\text{elec}}. \]

\[ \Gamma_{\text{vib}} \otimes \Gamma_{\text{elec}} = \Gamma_{\text{elec}} \otimes \Gamma_{\text{vib}} = \Gamma_{\text{elec}} \otimes \Gamma_{\text{vib}}. \]

Taking into account that for the ketene molecule \( \Gamma_{\text{elec}} = A_1 \), \( \Gamma_{\text{vib}} = A_1 \), and \( \Gamma_{\text{elec}} = B_1 \); that in the \( C_{2v}(M) \) molecular symmetry group \( \Gamma^* = A_2 \) and \( \Gamma^{(s)} = A_1 \); as well as that

\[ \Gamma_{\text{elec}} = \begin{cases} \Gamma^{(s)}, & \text{for } l \text{ even} \\ \Gamma^*, & \text{for } l \text{ odd} \end{cases} \]

where \( l \) is an angular momentum of the Rydberg electron (photoelectron), we rewrite Eq. (4) as
\[
\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} \otimes B_1 \otimes \Gamma^\text{vib} \otimes \Gamma^\text{rot} \otimes A_1 \otimes A_1 \otimes \Gamma^\text{vib} \otimes A_1, \text{ for } \begin{cases} l & \text{even} \\ l & \text{odd.} \end{cases}
\]

After simplifications, it takes the form
\[
\begin{pmatrix} B_1 \\ B_2 \end{pmatrix} \otimes \Gamma^\text{vib} \otimes \Gamma^\text{rot} \otimes \Gamma^\text{rot} \otimes A_1, \text{ for } \begin{cases} l & \text{even} \\ l & \text{odd.} \end{cases}
\]

Now, using Eq. (6) and Table 12-9 from Ref. 38, we write the rovibronic transition rules as follows

<table>
<thead>
<tr>
<th>Excited mode</th>
<th>Symmetry</th>
<th>(\Delta K_a)</th>
<th>(\Delta K_c)</th>
<th>(\Delta K_{\text{even}})</th>
<th>(\Delta K_{\text{odd}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1, v_2, v_3, v_4)</td>
<td>(a_1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>e</td>
</tr>
<tr>
<td>(v_5, v_6)</td>
<td>(b_1)</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>o</td>
</tr>
<tr>
<td>(v_7, v_8)</td>
<td>(b_2)</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>e</td>
</tr>
</tbody>
</table>

where \(o\) (e) stands for odd (even). Therefore, excitation of \(a_1\) modes (or \(A_1\) vibronic levels) of the ground electronic state of the ketene cation is governed by the \(\Delta K_{\text{even}}\) odd selection rule, while for \(b_1\) and \(b_2\) modes (or \(B_1\) and \(B_2\) vibronic levels) the \(\Delta K_{\text{even}}\) even selection rule is expected.

Both ketene isotopomers studied in this project, \(\text{CH}_2\text{CO}\) and \(\text{CD}_2\text{CO}\), transform in the \(C_{2v}\) (\(M\)) group. The hydrogen atoms are fermions (nuclear spin 1/2) and their odd permutation changes the sign of the total internal wave function, thus

\[
\Gamma^\text{vib} \otimes \Gamma^\text{rot} \otimes B_1(B_1) \quad \text{for } (+) \text{ parity.} \tag{7}
\]

The deuterium atoms are bosons (nuclear spin 1) and their odd permutation does not change the sign of the total internal wave function, thus

\[
\Gamma^\text{vib} \otimes \Gamma^\text{rot} \otimes A_1(A_2) \quad \text{for } (+) \text{ parity.} \tag{8}
\]

In normal ketene, \(\text{CH}_2\text{CO}\), the total nuclear spin can be equal to 1 or 0. There are four states of the total nuclear spin: three of them are symmetric and one is antisymmetric. In order to satisfy Eq. (7), the symmetric nuclear spin states can only combine with \(K_a\) = odd rovibronic states (\(B_1\) and \(B_2\) species, see Table 12-9 from Ref. 38), while the antisymmetric ones only combine with \(K_a\) = even rovibronic state (\(A_1\) and \(A_2\) species). The ratio of the statistical weights of the \(K_a^\text{even}\) to \(K_a^\text{odd}\) even levels is, thus, equal to 3:1. For deuterated ketene, \(\text{CD}_2\text{CO}\), the total nuclear spin can take values of 2, 1, and 0. There are six antisymmetric states of the total nuclear spin and three symmetric ones. Therefore, the ratio of statistical weights of the \(K_a^\text{even}\) to \(K_a^\text{odd}\) even levels in \(\text{CD}_2\text{CO}\) is equal to 3:6 = 1:2. Based on the value of the total nuclear spin, normal ketene is classified as ortho (odd nuclear spin) and \(\text{para}\) (even nuclear spin). The \(\text{ortho}\) normal ketene has only \(K_a^\text{even}\) odd levels, while the \(\text{para}\) ketene has only \(K_a^\text{even}\) even ones.

In our jet cooled molecular beam, only the lowest \(K_a\) levels of each species (\(\text{ortho}\) and \(\text{para}\)) are expected to be populated. Thus, in \(\text{CH}_2\text{CO}\), excitations originating from \(K_a^\text{even} = 1\) are expected to be three times as strong as those originating from \(K_a^\text{odd} = 0\). In \(\text{CD}_2\text{CO}\), transitions originating from \(K_a^\text{even} = 0\) are expected to be two times stronger than those originating from \(K_a^\text{odd} = 1\).

It was shown above that excitations of \(A_1\) vibronic levels of the cation obey the \(\Delta K_{\text{even}}\) odd selection rule. This will lead for \(A_1\) levels to three-band patterns in ZEKE or MATI spectra of jet-cooled ketene. For normal ketene, the \(K_a^\text{even} = 1\) band will be surrounded by a pair of three times stronger bands, the \(K_a^\text{odd} = 0\) band at the lower-wave number side and the \(K_a^\text{odd} = 2\) band at the higher-wave number side. Since the rotational constants of the cation are expected to be similar to those of the neutral ketene (see below), each of the three bands will show a strong unresolved \(Q\)-form branch \((N^+ - N^- = 0)\) surrounded by \([N^+ - N^-] > 0\) branches. Similarly, three corresponding bands are expected for \(\text{CD}_2\text{CO}\) with the middle one being twice as strong as the two side ones. The three bands may not be fully resolved since the \(A^+\) and \(A''\) rotational constants of deuterated ketene are about two times smaller than those of the ordinary ketene molecule. Excitation of the \(B_1\) and \(B_2\) vibrational levels of the ketene cation satisfies the \(\Delta K_{\text{even}}\) even selection rule. Two bands are expected to be present in the spectra, \(K_a^\text{even} = 0\) and \(K_a^\text{even} = 1\), which will be unresolved in both isotopomers since, as mentioned above, the rotational constants of the neutral and cation ground states are comparable.

The \(\tilde{X}^2B_1\) ground electronic state of the ketene cation has been predicted by \textit{ab initio} calculations to have \(C_{2v}\) symmetry and to have a similar geometric structure as the ground state of neutral ketene.\(^{8,31,40}\) The highest occupied molecular orbital in the ground state of neutral ketene is a doubly occupied \(2b_1\) orbital, which has predominantly \(\pi_{\text{C-0}}\) bonding character. The next highest occupied orbital, \(2b_2\), is bound by about 4 eV stronger than \(2b_1\). Thus, all Rydberg states below the first IP are expected to originate from an excitation of a \(2b_1\) electron.\(^{5}\)

A two-photon excitation of high-\(n^+\) Rydberg states of ketene promotes an electron from the highest occupied molecular orbital \(2b_1\),\(^{31}\) which is mostly \(p\) with some admixture of \(d\) character. For atom-like two-photon transition, \(\Delta l = 0, \pm 2\). Thus, the two-photon excitation may be described approximately as \(2p \rightarrow np, nf\) and \(2d \rightarrow ns, nd, ng\). In a two-photon transition, the total angular momentum quantum number has to satisfy the following condition:

\[
|\Delta J| = |J' - J''| = 0, \pm 1, \pm 2. \tag{9}
\]

Taking into account that \(J' = N^+ + 1\), where \(N^+\) is the total angular momentum of the cation core, while \(s\) and \(l\) are the spin and the orbital angular momenta of the Rydberg electron, respectively, and that only \(l \leq 4\) are possible in our experiment, we can rewrite Eq. (9) as

\[
|\Delta N| = |N^+ - J'| \leq 6.5. \tag{10}
\]

Since we expect to excite predominantly \(ns, np,\) and \(nd\) Rydberg states \((l \leq 2)\), we should observe in fully rotationally (and spin-rotationally) resolved spectra at most ten \((|\Delta N| \leq 4.5)\) branches.

In electronically allowed transitions, the strongest transitions are those for which the vibrational symmetry of the excited state is the same as that of the lower state. Since all transitions in our experiment originate from the ground vibrational level of \(A_1\) symmetry, the excitations of \(A_1\) sym-
metric vibrational levels of the ketene cation will be strongest. Further restriction on the strong transitions can be placed by analyzing characters of the normal modes. As mentioned, the $2b_1$ electron, which is excited in our experiment, has the $\pi_{\text{C-C}}$ bonding and $\pi_{\text{C-O}}$ antibonding character. Thus, those normal modes, which show large displacements in the C–C–O chain upon excitation, are expected to be strong. Takeshita\textsuperscript{40} analyzed character of $\alpha_1$ normal modes of CH$_2$CO$^+$ and CD$_2$CO$^+$. He showed that $\nu_3$ and $\nu_4$ vibrational modes of CD$_2$CO$^+$ are mixtures of C=C stretching and CD$_2$ scissoring motions, with $\nu_3$ being 58% CD$_2$ scissor and 40% C=C stretch and $\nu_4$ being 54% C=C stretch and 40% CD$_2$ scissor. He also showed that the $\nu_1$ mode is 90% C=O stretch and 10% C=C stretch, while the $\nu_2$ mode is almost pure (98%) C–H stretch. Thus, the $\nu_1$, $\nu_3$, and $\nu_4$ modes should appear strongly in our CD$_2$CO$^+$ spectrum. In CH$_2$CO$^+$, the $\nu_3$ and $\nu_4$ modes are almost pure CH$_2$ scissor (95%) and C=C stretch (93%) motions, respectively, $\nu_1$ is 100% C–H stretch, and $\nu_2$ is 90% C=O stretch and 10% C=C stretch. Therefore, in the CH$_2$CO$^+$ spectrum only $\nu_2$ and $\nu_4$ are expected to be present.

IV. DATA ANALYSIS AND RESULTS

A. Vibrational structure

Overview scans of vibrational spectra of the $X^2B_1$ electronic ground state of both ketene cations were recorded using the MATI scheme A by scanning the dye laser and detecting the MATI ions. Figures 2 and 3 show portions of the MATI spectra in the region of 77 300–80 000 cm$^{-1}$ for the CH$_2$CO$^+$ and CD$_2$CO$^+$ isotopomers, respectively. No spectral features were observed at higher wave numbers. For convenience, the wave numbers relative to the strongest feature near 77 530 cm$^{-1}$ (origin band) are shown on the second horizontal axis for both isotopomers. Wave numbers of several fundamental, overtone, and combination bands were determined from the spectra. They are listed in Tables I and II.

The spectrum of the ordinary ketene isotopomer (Fig. 2) shows three strong features. The strongest one near 77 530 cm$^{-1}$ is the origin band, 0$^0$. Vibrational features observed in our spectra are labeled by the upper vibrational level using the $i^n$ symbol, where $i$ indicates a vibrational mode, as in $\nu_i$, and $n^+$ is the number of quanta of the $\nu_i$ mode excited in the ground state of the cation. Labeling transitions by the upper level does not lead to any confusion, since all excitations occur from the zero-vibration level of the ground electronic state of the neutral ketene. The origin band has been studied by ZEKE as well as higher resolution MATI scheme B techniques and will be described in more detail later. The two other intense features at 1020(2) and 2227(2) cm$^{-1}$ are assigned as $4^1$ and $2^1$, that is, transitions to one quantum of the totally symmetric $a_1$ vibrations, $\nu_4$ (C=C stretch) and $\nu_2$ (C=O stretch), respectively. Excitation of the $\nu_3$ (95% CH$_2$ scissor) $a_1$ vibration is assigned to the weak feature at
1350(3) cm\(^{-1}\). It was not expected to be strong in the ordinary ketene as it has only 5\% of C–C stretch character.\(^\text{40}\) The fourth \(a_1\) vibration, \(v_1\) (100\% C–H symmetric stretch), could not be observed.

In the MATI spectrum of CD\(_2\)CO\(^{+}\), the strongest feature near the low-wave number end of the spectrum (see Fig. 3) is the origin band, 0\(^0\). The intense features at 91(6)\(^2\), 1094\(^2\), and 2243(2) cm\(^{-1}\) correspond to totally symmetric \(a_1\) vibrations and are assigned as 4\(^4\), 3\(^3\), and 1\(^1\) transitions, respectively. Observation of these excitations is consistent with the characters of the normal modes, as discussed above. The strong feature at 2207(2) cm\(^{-1}\) corresponds to two quanta of \(v_3\) vibration and is labeled as 3\(^2\). The strong features do not show any structure in MATI spectra, but are clearly resolved as triplets in the ZEKE spectra, which will be presented later.

In addition, there are several weak features in the spectra of both CH\(_2\)CO\(^{+}\) and CD\(_2\)CO\(^{+}\), which do not correspond to any of the \(a_1\) modes or their combinations. Their assignment has been aided by a reference to the experimentally determined vibrational wave numbers of the ground state of the neutral molecule.\(^\text{16}\) The assignments have also been verified by the isotope effect upon H–D substitution, which will be discussed in more detail later.

The weak features at 470(3) cm\(^{-1}\) in the spectrum of CH\(_2\)CO\(^{+}\) (Fig. 2) and at 447(5) cm\(^{-1}\) in the spectrum of CD\(_2\)CO\(^{+}\) (Fig. 3) are assigned as 6\(^1\), that is as the excitations of one quantum of the \(v_6\) mode of \(b_1\) symmetry. The corresponding wave numbers in the ground states of neutral CH\(_2\)CO and CD\(_2\)CO are equal to 528 and 435 cm\(^{-1}\), respectively. Similarly, the weak features at 745(3) cm\(^{-1}\) in the spectrum of CH\(_2\)CO\(^{+}\) (Fig. 2) and at 586(5) cm\(^{-1}\) in the spectrum of CD\(_2\)CO\(^{+}\) (Fig. 3) are assigned to the excitation

### Table I. Fundamental wave numbers (in cm\(^{-1}\)) of the \(X^2B_1\) ground state of CH\(_2\)CO\(^{+}\) and CD\(_2\)CO\(^{+}\).

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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1)</td>
<td>C–H sym.</td>
<td>3070.4</td>
<td>C–H sym.</td>
<td>3099</td>
<td>3288</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(v_2)</td>
<td>C=O (asym.)</td>
<td>2152.6</td>
<td>C=O (asym.)</td>
<td>2276</td>
<td>2596</td>
<td>2229</td>
<td>2226.5</td>
<td>2227(2)</td>
<td>2227(2)</td>
</tr>
<tr>
<td>(v_3)</td>
<td>CH(_3) scissor</td>
<td>1386.6</td>
<td>CH(_3) scissor</td>
<td>1378</td>
<td>1471</td>
<td>1378</td>
<td>1351.4</td>
<td>1350(3)</td>
<td>1350(3)</td>
</tr>
<tr>
<td>(v_4)</td>
<td>C=C (sym.)</td>
<td>1116.0</td>
<td>C=C (sym.)</td>
<td>1051</td>
<td>1049</td>
<td>1028</td>
<td>1021.4</td>
<td>1020(2)</td>
<td>1020(2)</td>
</tr>
<tr>
<td>(v_5)</td>
<td>CH(_2) wag</td>
<td>587.3</td>
<td>CH(_2) wag</td>
<td>764</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>745(3)</td>
<td>745(3)</td>
</tr>
<tr>
<td>(v_6)</td>
<td>C=C=O lin. bend</td>
<td>528.4</td>
<td>C=C=O lin. bend</td>
<td>466</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>470(3)</td>
<td>470(3)</td>
</tr>
<tr>
<td>(v_7)</td>
<td>C–H asym.</td>
<td>3165.4</td>
<td>C–H asym.</td>
<td>3218</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(v_8)</td>
<td>CH(_3) rock</td>
<td>977.8</td>
<td>CH(_3) rock</td>
<td>1014</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(v_9)</td>
<td>C=C=O lin. bend</td>
<td>439.0</td>
<td>C=C=O lin. bend</td>
<td>411</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>403(3)</td>
<td>403(3)</td>
</tr>
</tbody>
</table>

\(^{a}\text{Reference 16.}\)^{b}\text{Reference 32.}\)^{c}\text{Reference 40.}\)^{d}\text{Reference 31.}\)^{e}\text{This work.}\)^{f}\text{Numbers in parentheses indicate estimated maximum errors.}

### Table II. Wave numbers (in cm\(^{-1}\)) of the overtone and combination bands in the \(X^2B_1\) ground state of CH\(_2\)CO\(^{+}\) and CD\(_2\)CO\(^{+}\).

<table>
<thead>
<tr>
<th></th>
<th>CH(_2)CO(^{+})</th>
<th>CD(_2)CO(^{+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4^2)</td>
<td>2029(3)</td>
<td>3(^2)</td>
</tr>
<tr>
<td>(5^2)</td>
<td>1477(3)</td>
<td>5(^2)</td>
</tr>
<tr>
<td>(6^2)</td>
<td>930(10)</td>
<td>6(^2)</td>
</tr>
<tr>
<td>(9^2)</td>
<td>819(10)</td>
<td>3(^1)</td>
</tr>
<tr>
<td>(4^16^1)</td>
<td>1496(5)</td>
<td>5(^1)</td>
</tr>
<tr>
<td>(4^19^2)</td>
<td>1830(10)</td>
<td>...</td>
</tr>
</tbody>
</table>
patterns are expected for them. The 5^2 and 4^2 bands clearly show the expected three-band patterns. However, structures of the very weak 9^2 and 6^2 bands could not be determined. Assignments of other very weak features in Fig. 2, at 1496(5) and 1830(10) cm^{-1} as 4^1 6^1 and 4^1 9^2 bands, respectively, are uncertain. The feature at 1025(3) cm^{-1} in Fig. 3 is believed to be the 5^1 6^1 band, while that at 1690(3) cm^{-1} is the 3^1 5^1 band.

B. Rotational structure

As was discussed above, the triplet of the origin band in the MATI spectrum of CH_2CO^+ in Fig. 2 corresponds to the resolved K_a structure. The spacing between adjacent peaks of the triplet is equal to about 18 cm^{-1}, which is approximately equal to 2A'' (A'' = 9.4 cm^{-1}) is the rotational constant of the neutral ground state. If the rotational constant of the ground state of the cation A^+ has a value similar to A'', this observation is consistent with the ΔK_a = K_a'' - K_a' = odd selection rule predicted above. The three peaks of the triplet correspond to the 'Q_0 (K_a'' = 0 - K_a' = 1, ΔK_a = -1), 'Q_1 (K_a'' = 1 - K_a' = 0, ΔK_a = +1) and 'Q_3 (K_a'' = 2 - K_a' = 1, ΔK_a = +1) branches, where standard ΔKΔN_K notation is used. The intensities of the two side peaks (K_a'' = 1) were expected to be three times as strong as the intensity of the central one (K_a'' = 0). This intensity pattern is not observed in our MATI spectrum of CH_2CO^+. The deviation from the 3:1 ratio in the low resolution MATI spectrum is caused by an overlap of the lower wave number peaks with the red tails of the higher wave number ones. However, as will be shown later, the patterns observed in the higher resolution ZEKE and MATI (scheme B) spectra are in good agreement with the predicted 3:1 ratio.

At the higher wave number side of the origin band, two weak peaks at 77 610.6 and 77 667.3 cm^{-1} in Fig. 2 are apparent. These are the 'Q_0 (K_a'' = 3 - K_a' = 0, ΔK_a = 3) and 'Q_1 (K_a'' = 4 - K_a' = 1, ΔK_a = 3) branches. The intensities of the ΔK_a = +3 peaks are about 2 orders of magnitude lower than those of the ΔK_a = ±1 triplet, which indicates that the ketene cation in its ground electronic state is a near-symmetric top, just like the neutral species.

In the case of CD_2CO^+, the central peak of the triplet is expected to be twice as strong as the side peaks. As can be seen in Fig. 3, the resolution in the MATI spectrum (scheme A) is insufficient to resolve the three peaks of the triplet. For CD_2CO^+, the A rotational constant is about half of that for CH_2CO^+. Therefore, the spacings between the three peaks are about twice as small as those in CH_2CO^+. As will be shown later, the triplet is well resolved in the ZEKE spectrum and partially resolved in the high resolution MATI spectrum obtained using MATI scheme B.

The two other intense features in the MATI spectrum of CH_2CO^+, 4^1 and 2^1, also consist of three peaks. Since ν_4 and ν_2 are both totally symmetric (a_1) vibrations, the rotational structures of these two bands are expected to be similar to that of the origin band. The separations of the three peaks in each of the two bands are nearly identical to those in the origin band, which indicates that the A rotational constants of the 4^1, 2^1, and 0^0 vibronic levels are similar. The weak 3^1 band also shows a similar rotational structure to the origin band.

In order to determine the cation rotational constants and accurate ionization energies, high resolution MATI (scheme B) and ZEKE experiments have been performed. Figure 4 shows the TOF profile recorded using MATI scheme B. The first peak in Fig. 4 corresponds to the LR MATI signal, the peak in the middle corresponds to the HR MATI signal, while the third peak corresponds to the prompt (PR) ion signal. By gating the signal on the HR and LR peak, both the high resolution and low resolution MATI spectra were recorded simultaneously. Figure 5 shows the origin bands of the X̃^2B_1 ground electronic state of CH_2CO^+ recorded in HR MATI (trace a) and LR MATI (trace b) ion channels. For comparison, the spectrum of the origin band recorded using MATI scheme A is also shown in Fig. 5 (trace c). The triplet is fully resolved in the high resolution MATI spectrum [Fig. 5 (a)]. In the case of CD_2CO^+, weak shoulders are observed on both sides of the strong central peak of the origin band in the high resolution MATI spectrum.

Figures 6 and 7 (upper traces) show the ZEKE spectra of the origin bands of CH_2CO^+ and CD_2CO^+. The resolution of the ZEKE spectra was significantly higher than the resolution of either of the two MATI schemes. Nevertheless, it
where angular momentum quantum numbers; and the ‘‘\(\text{FIG. 7. ZEKE photoelectron spectrum of the origin band of CD}_2\text{CO}^+\)’’ bands of both isotopomers were fitted to the well known

\[ E = [A - \frac{1}{2}(B^+ + C^+)]K^2_a + \frac{1}{2}(B^+ + C^+)N^+ (N^+ + 1) - \frac{1}{2}(B^+ + C^+)J^+ (J^+ + 1), \]

was still insufficient to fully resolve the rotational structure. The partially rotationally resolved ZEKE spectra of origin bands of both isotopomers were fitted to the well known asymmetric top formula

where \(A\), \(B\), and \(C\) are rotational constants; \(K_a\), \(N\), and \(J\) are angular momentum quantum numbers; and the ‘‘\(\text{upper trace}\)’’ and \(\text{lower trace}\)’’ superscript indicates the cation (neutral) state. The ionization potentials as well as the \(A\) and \((B + C)/2\) rotational constants of the zero-vibration level of the \(\tilde{X}^2B_1\) state of CH\(_2\)CO\(^+\) and CD\(_2\)CO\(^+\) were obtained. The ionization potentials are equal to 77 539.4 \pm 2.0 and 77 534.3 \pm 2.0 \text{ cm}^{-1}; the \(A\) rotational constants are equal to 9.14(4) and 4.60(8) \text{ cm}^{-1}; and the \((B + C)/2\) rotational constants are equal to 0.339(6) and 0.27(18) \text{ cm}^{-1} for CH\(_2\)CO\(^+\) and CD\(_2\)CO\(^+\), respectively. The rotational constants of the ground state of the neutral molecule were fixed in the fits at the values from Ref. 10.

The spectra of the origin band of CH\(_2\)CO\(^+\) and CD\(_2\)CO\(^+\) were simulated using the parameters described above. The Maxwell–Boltzmann population distribution in the rotational levels of the neutral ground state characterized by the single rotational temperature of 6 K was assumed. The best overall agreement between simulated and experimental spectra was obtained with intensities of the \(|\Delta N| = |N^+ - J^+| > 1.5\) branches weighted by a \(1/|\Delta N|\) factor. The negligible intensity of \(|\Delta N| > 3.5\) branches supports our prediction that the Rydberg electron is excited from the \(2b_1\) orbital having predominantly \(p\) character. It also indicates that low angular momentum Rydberg states \((s\) and \(p)\) are excited. The simulated spectra are shown in Figs. 6 and 7 (lower trace).

V. DISCUSSION

Two vibrational modes, \(v_3\) and \(v_4\), are strongly excited in the \(\tilde{X}^2B_1\) state of CH\(_2\)CO\(^+\), with \(v_4\) being slightly stronger of the two. The fundamental wave number of the \(v_2\) mode in the ground state of cation, 2227(2) \text{ cm}^{-1}, is 3.3% larger than the corresponding wave number in the ground state of neutral ketene. The fundamental wave number of the \(v_4\) mode, 1020(2) \text{ cm}^{-1}, is 9.1% smaller in cation as compared with neutral ketene. These observations are consistent with the \(2b_1\) orbital in the ground state of neutral ketene being \(p_{C=C}\) bonding and \(p_{C=O}\) antibonding as well as with \(v_2\) and \(v_4\) being 90% \(C=O\) stretch/10% \(C=C\) stretch and 93% \(C=C\) stretch/7% \(C=O\) stretch in the cation, respectively.\(^{40}\) The \(v_3\) excitation (5% \(C=C\) stretch/95% CH\(_2\) scissor\(^{40}\)) is also present in CH\(_2\)CO\(^+\), but it is weak, as expected. In CD\(_2\)CO\(^+\), three strong excitations, \(v_1\), \(v_3\), and \(v_4\) are observed. As described in section II, all three modes contain significant \(C=C\) stretch and \(C=O\) stretch characters. The strongest band among the three is \(v_3\), followed by \(v_4\) and \(v_4\). Such the intensity pattern agrees with the \textit{ab initio} predictions\(^{40}\) indicating that the \(v_1\) mode in 90% \(C=O\) stretch and 10% \(C=C\) stretch in the cation; the \(v_1\) mode is 40% \(C=C\) stretch, 2% \(C=O\) stretch, and 58% CD\(_2\) scissor; while \(v_4\) is 54% \(C=C\) stretch, 5% \(C=O\) stretch, and 40% CD\(_2\) scissor. A similar intensity pattern, \(v_4\) stronger than \(v_3\) in CH\(_2\)CO\(^+\), but \(v_3\) stronger than \(v_4\) in CD\(_2\)CO\(^+\), was recently observed by Willitsch et al.\(^{32}\) The fundamental wave number of the \(v_1\) mode in the ground state of CD\(_2\)CO\(^+\), 2243(2) \text{ cm}^{-1}, is 5.5% larger than that of the corresponding mode \((v_2)\) in neutral ketene. The fundamental wave numbers of \(v_3\) and \(v_4\) of cation both are smaller than the corresponding wave numbers in the neutral ketene molecule. The \(v_3\) wave number, which is 40% \(C=C\) stretch in cation, is smaller by as much as 11.4%, while the wave number of the
The vibrational wave numbers of the \( v_1 \) and \( v_2 \) modes in CD\(_2\)CO\(^+\) are very similar according to the theoretical calculations,\(^{32,40}\) which has caused some difficulty in assigning the peak at 2243 cm\(^{-1}\) in Fig. 3. However, since the electron is ejected from the \( 2b_1 \) orbital of the \( \pi_{C=O}^\perp/\pi_{C=O} \) character, the C–D stretching mode is not expected to be active. The corresponding C–H stretching mode has not been observed in the spectrum of CH\(_2\)CO\(^+\) either. Thus, the peak at 2243 cm\(^{-1}\) in Fig. 3 can conclusively be assigned to \( v_1 \) (C=O stretch) vibrational mode.

The correctness of the assignment of the three totally symmetric vibrational modes can be assessed using the Teller–Redlich product rule.\(^{41}\) For the four totally symmetric \( a_1 \) vibrational modes of ketene cation, the product rule can be written as

\[
\rho(a_1) = \frac{D(a_1)}{\omega_1 \omega_2 \omega_3 \omega_4} = \frac{m_H}{M_H} \sqrt{M_D/M_H},
\]

where \( \omega_i \) are harmonic vibrational wave numbers, \( H \) and \( D \) indicate values for ordinary and deuterated ketene, \( m \) are atomic masses, and \( M \) are the total masses of the isotopomers. Using the fundamental wave numbers of the three vibrations measured in our experiment for each isotopomer and the \textit{ab initio} values for the remaining \( a_1 \) mode,\(^{40}\) we calculated the \( \rho(a_1) \) ratio to be equal to 0.530. The value predicted from the right-hand side of Eq. (12) is equal to 0.512. The good agreement of both values validates the assignment of the totally symmetric \( (a_1) \) vibrational modes. The small difference may result from the use of fundamental rather than harmonic experimental wave numbers. The fundamental wave numbers of the \( a_1 \) modes are in an excellent agreement with the recent results of Willitsch \textit{et al}.\(^{32}\) (see Table I).

In the low resolution photoelectron spectra of ketene studied in the past\(^{28,30,31}\) some intensity abnormalities were observed in both CH\(_2\)CO\(^+\) and CD\(_2\)CO\(^+\). Takeshita\(^{40}\) attributed the irregular intensity patterns to the superposition of \( 2^1 \) and \( 4^2 \) bands in CH\(_2\)CO\(^+\) and \( 1^1 \) and \( 3^2 \) bands in CD\(_2\)CO\(^+\). Niu \textit{et al}.\(^{31}\) argued that the Fermi resonance interactions were responsible for it. They claimed that in the case of CH\(_2\)CO\(^+\), \( 2^1 \) borrows intensity from \( 4^2 \), while in CD\(_2\)CO\(^+\), \( 3^2 \) borrows intensity from \( 3^4 \). At higher resolution of our MATI spectra (Fig. 2), the \( 4^2 \) band in CH\(_2\)CO\(^+\) is clearly separated from the \( 2^1 \) band. Similarly, the \( 3^2 \) band in CD\(_2\)CO\(^+\) appears next to the stronger \( 1^1 \) band, while the \( 3^4 \) band mentioned by Niu \textit{et al}.\(^{31}\) is absent from our spectra (Fig. 3). The \( 3^2 \) and \( 1^1 \) bands are better resolved in the ZEKE spectrum of CD\(_2\)CO\(^+\) (Fig. 8). Our MATI spectra also show that intensities of the \( \nu_4 \) progression in CH\(_2\)CO\(^+\) and the \( \nu_3 \) progression in CD\(_2\)CO\(^+\) decrease monotonically. Thus, our observations prove that the intensity abnormalities in the photoelectron spectra are due to the superposition of the \( 2^1 \) and \( 4^2 \) peaks in CH\(_2\)CO\(^+\) and \( 1^1 \) and \( 3^2 \) peaks in CD\(_2\)CO\(^+\).

In all previous studies of the ketene cation only totally symmetric vibrations have been observed. In our MATI spectra of CH\(_2\)CO\(^+\) and CD\(_2\)CO\(^+\), in addition to the totally symmetric vibrations discussed above, many weak features have been recorded. As shown in the previous section, they have been assigned to the \( 5^1 \), \( 6^1 \), and \( 9^1 \) bands as well as to overtone and combination bands. The \( \nu_5 \) and \( \nu_6 \) modes belong to the same \( b_1 \) symmetry type. The Teller–Redlich product rule for these two vibrations is given by Eq. (13)

\[
\rho(b_1) = \frac{D(b_1)}{\omega_5 \omega_6} = \frac{M_H}{M_H} \sqrt{M_D/M_H}.
\]

where \( \omega_i \) is the moment of inertia about the \( y \) axis and all other variables have the same meaning as in Eq. (12). Approximating the \( I_y \) values for the cations with the corresponding values of the neutral CH\(_2\)CO and CD\(_2\)CO isotopomers,\(^{42}\) we calculated the \( \rho(b_1) \) ratio from the right-hand side of Eq. (13) to be equal to 0.769. The \( \rho(b_1) \) value obtained from the fundamental wave numbers of \( b_1 \) vibrations measured from our spectra is equal to 0.748. The good agreement of the two values validates the assignments of the \( 5^1 \) and \( 6^1 \) bands. It also supports the claim that the geometric structure of the ground state of cation is similar to that of the neutral ketene molecule. The measured wave numbers of the \( \nu_5 \) and \( \nu_6 \) fundamentals also agree very well with the \textit{ab initio} results\(^{32}\) (see Table I).

The observed intensity patterns of the \( 5^1 \) and \( 6^1 \) bands in the CH\(_2\)CO\(^+\) and CD\(_2\)CO\(^+\) spectra suggest that although characters of the \( \nu_5 \) and \( \nu_6 \) modes are mixed, the \( \nu_6 \) mode in CH\(_2\)CO\(^+\) and the \( \nu_5 \) mode in CD\(_2\)CO\(^+\) can be best described as a C=C=O linear bend.

In the VUV ZEKE spectrum of CD\(_2\)CO\(^+\), Willitsch \textit{et al}.\(^{32}\) observed two weak peaks in addition to the one-quantum-excited totally symmetric \( a_1 \) modes. The peaks were tentatively assigned as \( 6^2 \) and \( 5^1 \) bands based on the results of their \textit{ab initio} calculations. They could not verify the assignment by an isotope effect as no corresponding peaks were observed in the spectrum of CH\(_2\)CO\(^+\). Our observation of \( 6^2 \) and \( 5^1 \) bands, in addition to the \( 5^1 \) and \( 6^1 \) fundamental excitations, for both isotopomers unambiguously verifies their assignment.
VI. CONCLUSION

The nonresonant two-photon MATI and ZEKE spectra of CH$_2$CO$^+$ and CD$_2$CO$^+$ have been recorded. Fundamental wave numbers of several (six for CH$_2$CO$^+$ and seven for CD$_2$CO$^+$) normal vibrational modes of the $\tilde{X}$2B$_1$ electronic ground state of both ketene cation isotopomers have been determined. The $\nu_5$, $\nu_6$, $\nu_8$, and $\nu_9$ nontotally symmetric vibrational modes have been observed in the $\tilde{X}$2B$_1$ state of the ketene cation for the first time. The higher resolution of MATI and ZEKE techniques as compared with the traditional photoelectron spectroscopy have made it possible to partially resolve the rotational structures of some of the bands. The rotational structure of the origin band and the totally symmetric vibrational bands is dominated by the three $\Delta K_a = \pm 1$ bands. The weak $\Delta K_a = + 3$ features are also observed in the origin band. The nontotally symmetric excitations follow the $\Delta K_a = 0$ selection rule. Rotational analysis of the ZEKE spectra have yielded the ionization potentials of the CH$_2$CO and CD$_2$CO isotopomers and the rotational constants for the ground state of the cations. The improved resolution has also allowed for the separation of 4$^2$ and 2$^1$ bands in CH$_2$CO$^+$ and 3$^2$ and 1$^1$ bands in CD$_2$CO$^+$, which has resolved the controversy of intensity abnormalities observed in the lower resolution photoelectron spectra. Our ionization potentials, vibrational wave numbers, and rotational constants agree very well with the values recently obtained by Willitsch et al.\textsuperscript{32}

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