Identification of individual conformers in C₄H₆O isomers using conformer-specific vibrational spectroscopy†

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We measured the conformer-specific vibrational spectra of C₄H₆O isomers in neutral and cationic states using IR resonant vacuum ultraviolet mass-analyzed threshold ionization (VUV-MATI) spectroscopy for the first time. Notably, the measured IR dip and hole-burn VUV-MATI spectra for each isomer represent the identifiable vibrational spectra of individual conformers in both states. Furthermore, we estimated the relative populations of individual conformers in crotonaldehyde (CA) and methyl vinyl ketone (MVK) isomers using the IR dip intensity, the corresponding Franck-Condon factor, and the IR absorption cross section. Our analysis revealed that the compositional ratio of s-trans to s-cis conformers in the CA isomer remained at 95.8 : 4.2 even under supersonic expansion, whereas that in the MVK isomer was determined as 90.6 : 9.4, which is consistent with previous research. These findings reveal that the conformational stability of each isomer depends on the position of the methyl group relative to the carbonyl group.

Introduction

The identification of individual conformers is typically performed using unique spectroscopic techniques capable of providing insights into the conformation-dependent reactivity of specific chemical reactions.¹⁻⁴ Such techniques reduce conformational complexity by utilizing the adiabatic cooling of molecules that results from supersonic expansion in the absence of the non-equilibrium kinetic effect.⁵⁻⁶ Subsequent investigations have revealed that molecules with a sufficiently low conformer interconversion barrier exist in conformational equilibrium even at low temperatures,⁷⁻⁹ whereas conformers with a high interconversion barrier retain their original composition during cooling via supersonic expansion.¹⁰⁻¹² For the former case, identifying peaks that correspond to a specific conformer in measured vibrational spectra requires additional exploration of the vibrational temperature-dependent conformational population, which, in turn, depends on the constructed potential energy surfaces associated with conformational interconversion. Nevertheless, deciphering the contribution of each conformer in the congested vibrational spectrum of a polyatomic molecule is still immensely difficult because of the comparable force fields between the atoms in conformers. As such, laser double resonance techniques such as hole-burning and IR depletion spectroscopies¹¹,¹⁴ have been suggested as alternative approaches to characterize the structures of individual conformers, although these techniques focus mainly on hydrogen-bonded clusters or van der Waals complexes in chromophore-containing systems, where resonance-enhanced multiphoton ionization (REMPI) is typically adopted.¹⁵⁻¹⁸ Meanwhile, for analyzing aliphatic species without an ultraviolet (UV) chromophore group, the IR vacuum ultraviolet (VUV) double resonance techniques that circumvent the limitations of REMPI have been developed, although excess VUV photon energy at 118 nm (the wavelength normally used) may cause uncontrollable fragmentations.¹⁹⁻²¹

α,β-Unsaturated carbonyl compounds that consist of an ethene conjugated to a carbonyl group, providing them with relatively high electrophilicity, have been researched extensively as an important precursor in reactions with nucleophiles as well as in astrochemical-relevant models of the interstellar medium.²²⁻²³ Interestingly, even simple precursors such as acrolein exhibit interconversion between s-trans and s-cis conformers, which manifests as rotation along the single bonds between ethene and carbonyl groups in the molecule. In principle, although the stereoselectivities of reactions depend on multiple environmental factors, the reaction pathway is affected primarily by the conformational preference in molecules, as described by the Diels-Alder reaction.²⁴ In addition, it has been reported that compounds with acrolein moiety undergo a variety of photochemical processes when in an excited state, which have prompted attempts to elucidate the photochemistry of conjugated enone molecules.²⁶⁻²⁸ These subsequent studies indicate that the photoproducts can be governed by the
conformational preference of the designated molecule in an electronic state. Therefore, the conformation responsible for photoreaction should be understood in terms of factors such as molecular orbital interactions and stabilization energies, which can be calculated by various theoretical models.29,30 Because of the importance of the methyl-substituted acrolein in both synthetic and atmospheric chemistry, the conformational stabilities and structures of s-trans and s-cis conformers are usually studied by substituting a methyl group in acrolein with crotonaldehyde (CA) and methyl vinyl ketone (MVK), of which conformational geometries are shown in Fig. 1.31–34 Before recent studies using single-photon vacuum ultraviolet mass-analyzed threshold ionization (VUV-MATI) spectroscopy and the Franck-Condon (FC) simulations,9,10 most investigations involving the conformations of these two isomers only examined the temperature-dependence of the peaks corresponding to each neutral conformer in vibrational or rotational spectra. This contributed to the fact that CA and MVK have very short lifetimes, that is, a few hundred femtoseconds, in the excited electronic state owing to the substituent effect of the methyl group on electronic relaxation rates.35 Most spectral analyses are consistent in finding that the s-trans conformer is more stable than the s-cis conformer despite the deviations in their relative stabilities. However, the theoretical predictions regarding the preferential conformation for MVK were inconsistent with the recent experimental results, suggesting that the uncertainty in the calculated energy values can originate from the use of incorrect functions and/or densities.9 Consequently, we were motivated to obtain identifiable vibrational spectra of individual conformers (i.e., s-trans and s-cis) in the two isomers, and thus provide indisputable experimental data regarding the conformational populations while also elucidating how the conformational stabilities in the two isomers change relative to the position of the methyl group.

![Fig. 1](image1.png) Geometries of s-trans and s-cis conformers in (a) CA and (b) MVK isomers.

**Experimental**

Experiments were performed using a homebuilt VUV-MATI spectrometer, the details of which have been provided in previous studies.36,37 A coherent and tunable VUV laser pulse with a wavelength range of 126.3–128.6 nm was generated by resonant four-wave difference frequency mixing (FWDFM) based on 4p6–5p[1/2]0 or 4p6–5p[5/2]2 transitions in Kr, which were alternated to avoid wavevector mismatches depending on the VUV wavelength. The MATI ion signals were normalized using the power of the tunable visible laser that was used for the FWDM-based VUV generation. For the IR resonant VUV-PI/MATI scheme, high-resolution IR laser light in the range of 2670–3100 cm⁻¹ with an approximate energy of 7 mJ per pulse...
was generated using a narrowband optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision, C24 0.1 cm /C0 1) pumped by a Nd:YAG laser seeded with a wavelength of 1064 nm. Next, the generated IR laser light was cylindrically focused using a telescope consisting of two CaF2 lenses (f = 75 and /C0 100 mm) and aligned perpendicularly to both the molecular beam and the ion-light direction into the photoionization chamber. The VUV laser pulse was delayed by approximately 5 ns with respect to the IR laser pulse, which photoexcites the neutral conformers to a vibrational state. The frequencies of all lasers used in the experiments were measured and calibrated using a wavemeter (HighFinesse, Wavelength Meter WS5) with an accuracy of 0.1 cm /C0 1.

Results and discussion

As shown in Fig. 2(a), the VUV-MATI spectra of the MVK and CA isomers, which are essentially the vibrational spectra of the two

isomers in the D0 state, were measured as a function of the VUV photon energy. The two most intense peaks, at 77 861 and 78 638 cm /C0 1, correspond to the 0–0 bands of MVK and CA, respectively, which is consistent with the respective adiabatic ionization energy (AIE) values of 77 867 ± 4 and 78 640 ± 3 cm /C0 1 determined in previous studies by extrapolating to the zero-field limit of the MVK and CA using VUV-MATI spectroscopy.9,10 At present, other than using FC simulations to determine the ionization thresholds of MVK and CA, respectively, was
Table 1  Vibrational assignment (in cm$^{-1}$) of individual conformers for the MVK and CA isomers in the S$_0$ state

| Mode$^a$ | IR + VUV | IR dip | Ref$^b$ | Calc$^c$ | Mode description$^d$ |
|---------|---------|--------|---------|---------|-----------------------|
| **MVK** |         |        |         |         |                       |
| s-trans ($C_h$) |         |        |         |         |                       |
| 5$^1$ | 2934 | 2949 | 2916 | CH$_3$ sym stretch |
| 19$^1$ | 2977 | 2980 | 2969 | Out-of-plane methyl CH stretch |
| 3$^1$ | 3018 | 3018 | 3019 | In-phase terminal CH$_2$ stretch |
| 2$^1$ | 3042 | 3072 | 3040 | Central C-H stretch |
| 1$^1$ | 3103 | 3103 | 3096 | Out-of-phase terminal CH$_2$ stretch |
| s-cis ($C_s$) |         |        |         |         |                       |
| 5$^1$ | 2925 | 2935 | 2908 | CH$_3$ sym stretch |
| 19$^1$ | 2964 | 2964 | 2956 | Out-of-phase methyl CH stretch |
| 4$^1$ | 3018 | 3017 | 3018 | Out-of-phase vinyl CH stretch |
| 2$^1$ | 3030 | 3061 | 3033 | Vinyl C-H breathing |
| 1$^1$ | 3109 | 3109 | 3106 | Out-of-phase terminal CH$_2$ stretch |
| **CA** |         |        |         |         |                       |
| s-trans ($C_h$) |         |        |         |         |                       |
| 5$^1$ | 2724 | 2724 | 2722 | 2775$^e$ | Carbonyl CH stretch |
| 9$^2$ | 2805 | 2805 | 2805 | 2741$^e$ | Overtone of carbonyl CH bending |
| 4$^1$ | 2931 | 2931 | 2932 | 2918 | CH$_3$ sym stretch |
| 19$^1$ | 2957 | 2957 | 2958 | 2957 | Out-of-phase methyl CH stretch |
| 3$^1$ | 2986 | 2986 | 2990 | 2999 | In-phase methyl and z-CH stretch |
| 2$^1$ | 3007 | 3007 | 3008 | 3017 | Out-of-phase methyl and z-CH stretch |
| 1$^1$ | 3048 | 3050 | 3054 | z-C--C(=O)--H stretch |
| s-cis ($C_s$) |         |        |         |         |                       |
| 5$^1$ | 2745 | 2795$^e$ |         |         | Carbonyl CH stretch |
| 9$^2$ | 2834 | 2768$^e$ |         |         | Overtone of carbonyl CH bending |
| 4$^1$ | 2928 | 2916 | CH$_3$ sym stretch |
| 19$^1$ | 2953 | 2955 | 2998 | Out-of-phase methyl CH stretch |
| 3$^1$ | 2980 | 2980 | 2998 | In-phase methyl and z-CH stretch |

$^a$ Mulliken notation. $^b$ Gas-phase IR spectrum from ref. 33. $^c$ Harmonic vibrational frequencies calculated from the optimized geometries with $C_s$ symmetry at the B3LYP/aug-cc-pVTZ level. $^d$ Vibrational assignment reported in ref. 33. $^e$ Peaks split by the Fermi resonance between the carbonyl CH stretching and overtone of carbonyl CH bending.

scanned. The IR absorption spectra of the MVK and CA in the S$_0$ state are shown in Fig. 3(a) and 4(a), respectively. The vibrational peaks corresponding to individual conformers in the IR absorption spectrum of each isomer might be identified using the simulated IR spectrum of each conformer in the S$_0$ state, with this process repeated for the MATI spectra. Accordingly, the conformer-specific vibrational spectra of the neutral isomer, that is, the IR dip VUV-MATI spectra of MVK and CA, were recorded by monitoring the 0–0 bands at 77 861 and 78 638 cm$^{-1}$ that were observed in the VUV-MATI spectra while scanning the frequency of the IR laser (Fig. 3(b) and 4(b)). The measured IR dip spectra are expected to be a proxy for the vibrational spectra of the stable s-trans conformers for the two isomers in the S$_0$ state. To check this, the IR spectra of the s-trans and the s-cis conformers in each isomer were simulated at various calculation levels using the aug-cc-pVTZ basis set, as shown in Fig. S1 and S2. All simulated vibrational frequencies were scaled to compensate for the uncertainties caused by the vibrational anharmonicity and the incomplete treatment of electron correlation, which are artifacts of using finite basis sets. Based on the simulated IR spectra (Fig. 3(c) and 4(c)) that agreed most closely with the experimental spectra, peaks observed in the IR dip spectra can be successfully assigned to the fundamental vibrational modes characterizing the C–H stretching vibrations of the s-trans conformer of each isomer (Table 1). As mentioned above, this implies that the measured IR dip spectra correspond to the identifiable vibrational spectra of the s-trans conformers for the two isomers in the S$_0$ state.

Furthermore, the distinct peaks observed at 3018 and 3103 cm$^{-1}$ in the IR dip spectrum of the s-trans conformer in MVK (Fig. 3(b)) matched closely with the peaks observed in the IR absorption spectrum of MVK (Fig. 2(a)). The prominent peaks at 2724, 2805, 2931, 2957 and 3007 cm$^{-1}$ in the IR dip spectrum of the s-trans conformer in CA (Fig. 4(b)) are also observed in Fig. 4(a). Notably, previous research indicates that the splitting of the two intense peaks at 2724 and 2805 cm$^{-1}$ corresponds to the Fermi resonance between the C(=O)–H stretching and the overtone of C(=O)–H bending.

The characteristic peaks (i.e., the 1(a') and 5(a') modes) at 3103 and 2724 cm$^{-1}$ isolated in the IR dip spectra of the s-trans conformers in MVK and CA were utilized in the IR hole-burn VUV-MATI scheme to acquire the identifiable vibrational spectra of the s-trans conformers for the two isomers in the D$_0$ state. This scheme is based on the fact that when the frequency...
Comparison of the relative populations and stabilities of individual conformers in the MVK and CA isomers obtained in this work with those reported in previous studies

| Method | s-trans | s-cis | Stability | Calc | Mode description |
|--------|---------|-------|-----------|------|------------------|
| MVK
This work | 90.6% | 9.4% | 53 cm⁻¹ | 77,867 ± 4 (0) | 0-0 band |
VUV-MATI | 88% | 12% | 48 ± 18 cm⁻¹ | 78,640 ± 3 (0) | In plane C-C=O bend |
IR | 76% | 24% | 45 cm⁻¹ | 78,853 (215) | In plane C=C-C bend |
IR and Raman | 69% | 31% | 162 cm⁻¹ | 79,105 (463) | In plane C=C-C bend |
CA
This work | 95.8% | 4.2% | 706 cm⁻¹ | 78,734 ± 3 (96) | 0-0 band |
VUV-MATI | 96.5% | 3.2% | 634 cm⁻¹ | 78,534 (315) | In plane C=C-C bend |
IR and Raman | 69% | 31% | 162 cm⁻¹ | 78,984 (344) | In plane C=C-C bend |

a Values reported in ref. 9 and 10 for MVK and CA, respectively. b Conformational geometries with C₂ symmetry at B3LYP/aug-cc-pVTZ level. c Vibrational assignments for MVK and CA reported in ref. 9 and 10, respectively. d Harmonic vibrational frequencies calculated from the optimized geometries with C₂ symmetry at B3LYP/aug-cc-pVTZ level. e Mulliken notation. f Values in parentheses indicate the ion internal energies of vibrational peaks estimated with respect to the 0-0 band positions of individual conformers.
the characteristic peaks (i.e., the 19(a') and 5(a') modes) at 2964 and 2745 cm$^{-1}$ isolated in the IR dip spectra of the s-cis conformers for the MVK and CA isomers in the S$_0$ state. Despite their low intensity, distinct peaks corresponding to the 0–0 bands of the s-cis conformers were observed in the IR hole-burn spectra of the MVK and CA at 78 217 and 78 734 cm$^{-1}$, respectively (Fig. 2(d)). In addition, the 0–0 band positions for the s-cis conformers in the two isomers corroborated the AIE values determined in previous studies. The assignments of the peaks observed in the IR hole-burn spectra of the individual conformers in the two isomers are listed in Table 2 alongside the calculated results and previously reported values. Owing to the vibrational excitations for the s-cis conformers of MVK and CA in the S$_0$ state, the 0–0 band signals were depleted by 4.3% and 20.9%, respectively.

We used the conformer-specific vibrational spectra of the MVK and CA isomers measured via IR dip and hole-burn VUV-MATI spectroscopy to estimate the relative amounts of the s-trans and the s-cis conformers in the S$_0$ state for MVK and CA. When a molecule absorbs the IR photon of high frequency, the intramolecular vibrational relaxation (IVR) from the initially excited vibrational mode can occur to other low-frequency modes. Hence, we utilized the sharp dips in the IR dip VUV-MATI spectra so that the possibility of the IVR process is maximally excluded. Then, assuming that the vibrational excitation-induced conformer population reduction determined via IR absorption reflects the hole-burn in the MATI ion signal produced by the conformer, the relative populations of two conformers can be determined using the dip intensities in their respective IR dip spectra; these intensities should be divided by the FC-factor related to the 0–0 band and the IR absorption probability of vibrational excitation corresponding to the dip frequency. The dip intensities were estimated by fitting the data using the single Gaussian function. To estimate the relative conformer populations in MVK, vibrations 1 and 19 at 3103 and 2964 cm$^{-1}$ for the s-trans and the s-cis conformers, respectively, were chosen. Then, the dip intensities were divided by FC-factors of 1.56 (s-trans) and 1.88 (s-cis) and IR absorption probabilities of 7.2 (s-trans) and 8.0 (s-cis). Thus, the relative populations of two conformers were determined as 90.6% (s-trans) and 9.4% (s-cis), which agree closely with previous values of 88% and 12%, which were determined by one-photon VUV-MATI spectroscopy. Similarly, we determined the relative conformer populations in CA by using vibrations 5 and 5 at 2724 (s-trans) and 2735 cm$^{-1}$ (s-cis), assuming no Fermi resonance-induced changes in intensity. The corresponding FC factors and IR absorption probabilities were 0.38 and 635 (s-trans) and 0.37 and 1052 (s-cis), leading to the relative amounts of the two conformers in CA being calculated as 95.8% (s-trans) and 4.2% (s-cis), which are in excellent agreement with those reported for one-photon VUV-MATI spectroscopy: 96.5% and 3.5%, respectively. These results are summarized in Table 3.

The difference in the relative conformational preferences for the MVK and CA isomers can be attributed to the extent to which the highest occupied molecular orbitals, which consist of nonbonding orbitals on the oxygen atom in the carbonyl group interacting with the σ orbitals in the molecular plane, are stabilized. This depends on the position of the methyl group. Stabilization between the σ orbitals and lone-pair p orbital of the oxygen atom occurs through hyperconjugation. Therefore, the stability of the s-cis conformer in MVK is expected to be higher than that in CA because of the interaction between the carbonyl and methyl groups, as shown in Fig. 3 and 4.

Conclusions

Conformers have similar vibrational structures both in the S$_0$ and D$_0$ states due to the comparable force fields between their nuclei. This has led to the continuous development of vibrational spectroscopic techniques to rigorously identify individual conformers of the designated molecule but only in the S$_0$ state. Our results demonstrate that the IR hole-burn VUV-MATI spectra of individual conformers in the D$_0$ state allow the VUV-MATI spectrum of a molecule to be rigorously deciphered, while the IR dip VUV-MATI spectra correspond to identifiable IR absorption spectra of individual conformers in the S$_0$ state. Therefore, we expect that these conformer-specific vibrational spectroscopies will become a highly effective spectroscopic technique to elucidate the conformational structures of a molecule in the S$_0$ and D$_0$ states.

Conflicts of interest

There are no conflicts to declare.

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