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ABSTRACT

We present here a synchrotron radiation vacuum ultraviolet photoionization study of the simplest alkoxy radical, CH_3O, a key reaction intermediate in atmospheric and combustion chemistry. A microwave discharge fast flow tube connected to a molecular beam sampling system is employed as a chemical reactor to initiate reactions and generate radicals. The CH_3O^+ cation from direct ionization of the CH_3O radical is detected successfully in the photoionization mass spectrum close to its ionization threshold. In addition, after identifying and removing the contribution of the ^{13}C-isotopic formaldehyde $H_2{}^{13}CO$ with the same isobaric mass $m/z = 31$, the high-resolution threshold photoelectron spectrum of CH_3O is obtained and assigned with the aid of calculated Franck–Condon factors. The adiabatic ionization energy of CH_3O is determined at 10.701 eV with an accuracy of 0.005 eV.

I. INTRODUCTION

Alkoxy radicals are key reaction intermediates and play essential roles in atmospheric and combustion chemistry.[1] In the atmosphere, they are formed by the oxidation of volatile organic compounds (VOCs) and can undergo isomerization, unimolecular dissociation, and bimolecular reactions, making them key players in the formation of secondary pollutants such as ozone and secondary organic aerosols.[2–4] The methoxy radical, CH_3O, is the simplest and the most important alkoxy radical, mainly formed by the oxidation of CH_4 in the atmosphere. As a result, the kinetics, spectroscopy, and dynamics of CH_3O have received a great deal of attention over the past decades.[1,3]

Various theoretical and experimental methods were applied to study the CH_3O radical and its deuterated analog CD_3O.[5–9] CH_3O has a C_{3V} symmetry in the X^2E ground state with an electronic configuration of $(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1e)^4(5a_1)^2(2e)^3$. The degenerate X^2E ground state is subject to Jahn–Teller distortions along the e vibrational modes, distorting into two Cs symmetric states ($^2A'$ and $^2A''$), with a splitting energy calculated at ~270 cm^{-1}.[10–12] In ionization transitions, removing an electron from the outermost $2e$ orbital can generate the CH_3O^+ cation into the X^3A_2, a^1E, and b^1A_1 states, where the singlet excited states are not stable and can rearrange to the isomer CH_2OH^+.[5,7]

The measurement of the ionization energy of CH_3O appears to be very challenging due, for instance, to the presence of the CH_2OH isomer that can contribute to the photoionization efficiency (PIE) curve. Ruscic and Berkowitz and Kuo *et al.* chose to turn toward deuterated CD_3OH + F as a precursor to overcome this issue and found an adiabatic ionization energy (AIE) for CD_3O of 10.726 ± 0.008[8] and 10.74 ± 0.02 eV[5] by photoionization mass spectrometry (PIMS). Ruscic and Berkowitz also derived a tentative photoelectron spectrum by differentiation of the modeled PIE.[8] Later, by HeI photoelectron spectroscopy (PES), the AIE of CH_3O was reported at 10.72 ± 0.01[6] and 10.78 ± 0.02 eV.[7] Table I compiles the ionization energies available in the literature. Previous results show that

TABLE I. Adiabatic ionization energies (AIEs) of CH_3O and related species.

Radicals	AIEs (eV)
CH_3O	10.72(1),[6] 10.78(2),[7] 10.715(8),[a] 10.701(5)[b]
CD_3O	10.72(1),[6] 10.74(2),[5] 10.726(8),[8] 10.729[c]
CH_2OH	7.56(1),[17,18] 8.14(1)[d,17,18]

[a]The calculated result with the ATcT recommended $\Delta_f H^0_{0\,K}(CH_3O) = 28.85 \pm 0.29$ kJ mol^{-1} and $\Delta_f H^0_{0\,K}(CH_3O^+) = 1062.74 \pm 0.75$ kJ mol^{-1}.[19]
[b]The present TPES result.
[c]The AIE of CD_3O has been calculated in this work to be 28 meV above that of CH_3O (see the text for details).
[d]The vertical ionization energy.

the CH_3O^+ cation possesses, as the neutral, a C_{3V} symmetric structure and that its optimized geometry is very similar to the one of the neutral CH_3O radical, except for the C–O bond length, decreasing slightly from 1.386 Å to 1.309 Å upon ionization.[9] Therefore, the C–O stretching mode of CH_3O^+ is expected to be excited upon ionization, and its vibrational frequency was theoretically predicted at 1279 cm^{-1} [8] and experimentally measured at 1950 cm^{-1} by Zhu *et al.* via HeI PES.[7]

Photoelectron spectroscopy has been shown to give a more accurate picture of the spectroscopy of the cation than PIE[13,14] and also of the thermochemical values such as AIEs or appearance energies. Furthermore, modern threshold photoelectron spectroscopy provides a higher and constant resolution that can be used to give more precise and accurate values by comparison with *ab initio* methods. In this work, we present a vacuum ultraviolet (VUV) photoionization study of CH_3O using double imaging photoelectron photoion coincidence (i^{2}PEPICO) spectroscopy.[15] The mass-selected high resolution threshold photoelectron spectrum (TPES)[14,16] corresponding to the CH_3O radical has been obtained, after removal of the $H_2{}^{13}CO$ contribution having the same isobaric mass. Then with the aid of the calculated Franck–Condon (FC) factors, the TPES has been assigned and the AIE of the CH_3O radical is determined with a higher accuracy than previously reported values.

II. EXPERIMENTAL SETUP

The experiments were performed on the undulator-based DESIRS beamline with the i^{2}PEPICO spectrometer, DELICIOUS III, at synchrotron SOLEIL. The beamline configuration and the i^{2}PEPICO spectrometer have been introduced previously, and only a brief description is provided here.[15,20] Synchrotron radiation photons, with linear horizontal polarization, were dispersed by a 6.65 m normal incidence monochromator from which a 200 l mm^{-1} grating was adopted to provide high photon flux and energy resolution of ~3 meV with the chosen slit width. A gas filter located upstream of the beamline and filled with Ar was utilized to eliminate high harmonics from the undulator.[20]

A fast flow tube mainly including a main tube and a collinear sliding injector was installed inside the source chamber of SAPHIRS, a permanent molecular beam end-station on the beamline, and acted as a chemical reactor to initiate reactions and generate radicals.[21–23] Fluorine atoms were produced from diluted F_2 gas in helium (5%, 10 SCCM) with a microwave discharge generator (2.45 GHz, Sairem GMP03 KSM) and fed into the flow tube. After adding methane (30 SCCM) and oxygen (600 SCCM), together with helium carrier gas (1100 SCCM), the methyl radical (CH_3) and the methyl peroxy radical (CH_3O_2) were produced through the reactions[23]

$$F + CH_4 \rightarrow CH_3 + HF, \quad (1)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M, \quad (2)$$

where M represents the species removing the internal energy of CH_3O_2 by collisions. The pressure inside the flow tube was monitored by a capacity gauge and presently fixed at 2 Torr by a closed-loop feedback throttle valve.

Inside the flow tube, the bimolecular reaction between CH_3 and CH_3O_2 and the self-reaction of CH_3O_2 could generate the CH_3O radical as follows:

$$CH_3 + CH_3O_2 \rightarrow CH_3O + CH_3O, \quad (3)$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3O + CH_3O + O_2. \quad (4)$$

This method avoids the presence of CH_3OH as a precursor (contrary to using F + CH_3OH),[5,6,24] which would make the measurements more challenging due to saturation (CH_3OH having an ionization energy very close to that of CH_3O).[25] The reaction of CH_3O with O_2 will lead to HO_2, while other radical–radical reactions such as the self-reactions of CH_3 and CH_3O or the fast reaction of CH_3O with HO_2 will also take place.[4,26] The major reactions undergoing in the flow tube are listed in Table S1.

After passing through two skimmers (1 mm diameter), the gas mixture in the flow tube was sampled and entered the ionization chamber of SAPHIRS, crossing the photon beam with a right angle.[21–23] The electrons and ions formed by photoionization at the center of DELICIOUS III were extracted and accelerated in opposite directions toward an electron velocity map imaging device and a modified Wiley–McLaren ion time-of-flight (TOF) 3D-momentum imaging analyzer and detected in coincidence via two position sensitive detectors (PSDs).[15] Electron images were filtered by the coincident ion mass-selection and position-selection to separate from background gas,[21] and an Abel inversion algorithm, pBasex, was utilized to provide the PES.[27]

III. RESULTS AND DISCUSSION

Figure 1 shows the photoionization TOF mass spectrum integrated in the 9.7 eV–11.5 eV energy range. Almost all the species listed in Table S1, except those with ionization energies above 11.5 eV, have been detected. For example, the three intense peaks at m/z = 15, 30, and 47 are assigned as the CH_3 radical, formaldehyde (H_2CO), and the CH_3O_2 radical,[23] where H_2CO can be produced from the $CH_3O + O_2$, $CH_3 + CH_3O$, $CH_3O + CH_3O_2$, and $CH_3O_2 + CH_3O_2$ reactions. The ethane (C_2H_6) product from the self-reaction of CH_3 leads to the same isobaric mass as H_2CO, but its ionization energy located at 11.56 eV is beyond the present energy range so does not contribute to the m/z = 30 peak.[25,28] Other peaks are also observed in the mass spectrum and are assigned, i.e., m/z = 28 (ethene, C_2H_4), 32 (methyl alcohol, CH_3OH), 46 (dimethyl ether, CH_3OCH_3), and 48 (methyl peroxide, CH_3OOH).

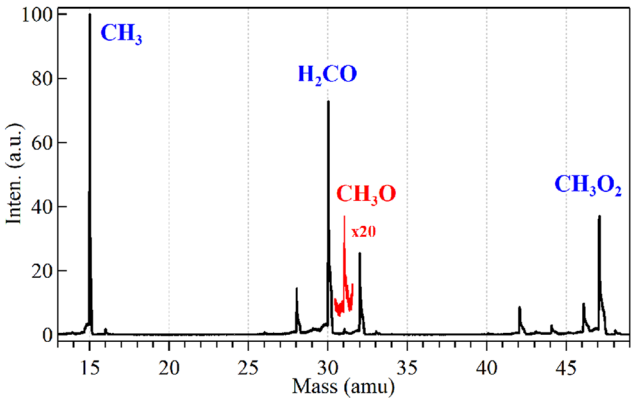

FIG. 1. Photoionization TOF mass spectrum integrated in the 9.7 eV–11.5 eV energy range, with 20 times magnified data in red to show the existence of CH_3O.

In particular, as shown in the magnified data in Fig. 1, the mass peak at m/z = 31 is assigned as the CH_3O^+ cation from direct ionization of CH_3O, close to its ionization threshold, although with a very weak signal. This channel carries contributions from $H_2{}^{13}CO$, and possibly from CH_2OH, although the energy range of this work precludes verification of the latter (see below).

The mass-selected photoelectron kinetic energy matrix corresponding to the m/z = 31 cation, as a function of photoelectron kinetic energy (eKE) and photon energy, was measured by scanning the synchrotron photon energy with a step size of 10 meV and is presented in Fig. 2(a). The integration of the matrix over all photoelectron kinetic energies yields the PIE curve, which has been added as a gray dashed line. As shown in Fig. 2(a), in the matrix, direct photoionization processes appear as a diagonal line with a unity slope,

$$eKE = h\nu - IE_{th}, \tag{5}$$

where IE_{th} is the ionization energy of a cationic state.

The mass-selected TPES is acquired by integrating the photoelectron signal $A(h\nu, KE)$ along constant cationic states (diagonal lines), up to a maximum value KE_{max}, according to the following expression:[29,30]

$$TPES(h\nu) = \int_0^{KE_{max}} A(h\nu + KE, KE)dKE. \tag{6}$$

The TPES records the signal of near-zero kinetic energy photoelectrons (KE_{max} = 100 meV) to get an intense signal, which is beneficial to the analysis of very diluted species, while its energy resolution (~20 meV) is comparable to that of the traditional TPES with subtraction of the hot electron contribution.[13,31]

Figure 2(b) shows the mass-selected TPES corresponding to the m/z = 31 cation. As also visible directly from the matrix, two vibrational bands with their peaks at $h\nu$ = 10.701 eV and 10.880 eV are observed, the second band with a larger intensity than the first one in the TPES. Previous calculations show that the CH_3O^+ cation possesses a similar structure as the neutral CH_3O radical,[9] so that the 0–0 adiabatic transition should correspond to the highest intensity peak in the PES. This is apparently not the case in the TPES of Fig. 2(b), whose unexpected shape therefore deserves a deeper analysis.

The hydroxymethyl radical (CH_2OH) is the most stable isomer of the CH_3O radical, and it may contribute to the TPES too. However, the AIE and the vertical ionization energy (VIE) of CH_2OH

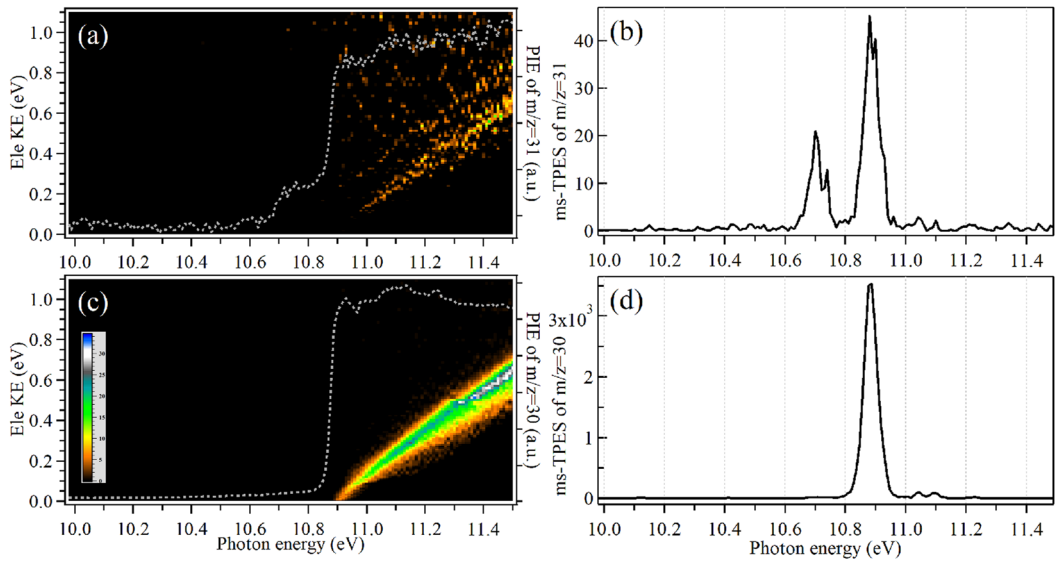

FIG. 2. Mass-selected photoelectron kinetic energy matrices and threshold photoelectron spectrum (TPES) corresponding to the [(a) and (b)] m/z = 31 and [(c) and (d)] m/z = 30 cations, together with their photoionization efficiency (PIE) curves marked with gray dashed lines. The inserted panel indicates that the signal intensity of the matrices increases from yellow to white, black being zero.

were measured at 7.56 ± 0.01 eV and 8.14 ± 0.01 eV,[17,18] respectively, far away from the present energy range. Moreover, the first excited state of CH_2OH^+ (a triplet state) is calculated at 3.9 eV above the singlet ground state at the M06-2X/AVTZ level by using the *Gaussian* 16 program package,[32] so that a VIE of the excited state of CH_2OH^+ would lie around 12 eV, more than 1 eV above the peaks we are observing. Therefore, the contribution of CH_2OH to our spectrum can be ruled out but not its presence in the reactor.

The ^{13}C-isotopic formaldehyde $H_2{}^{13}CO$ with a natural abundance of 1% of $H_2{}^{12}CO$ has the same isobaric mass (m/z = 31) as the CH_3O radical and might also contribute to the mass-selected TPES in Fig. 2(b). To demonstrate this, the mass-selected photoelectron kinetic energy matrix corresponding to formaldehyde (H_2CO, m/z = 30) was measured and is presented in Fig. 2(c). Figure 2(d) shows the mass-selected TPES of H_2CO in which an intense vibrational origin (0–0) peak is observed at $h\nu$ = 10.890 eV, in very good agreement with the literature AIE of H_2CO (AIE = 10.8887 ± 0.0005 eV).[33] The first band of the TPES of H_2CO therefore overlaps with the second band of Fig. 2(b), indicating that the ^{13}C-isotopic formaldehyde $H_2{}^{13}CO$ contributes to the mass-selected TPES of m/z = 31 too.

By subtracting 1% of the TPES of H_2CO, i.e., the ^{13}C-isotopic formaldehyde $H_2{}^{13}CO$ contribution, from the mass-selected TPES of m/z = 31 and assuming a constant ion detection efficiency between m/z = 30 and m/z = 31, the TPES of the CH_3O radical without interferences from other species was retrieved, as presented in Fig. 3(a). Two vibrational bands can be observed in the TPES with now, after subtraction, a reduced intensity of the second band, coherent with the expected Franck–Condon factor-driven vibrational distribution. Note that the subtraction induced a slightly worse signal-to-noise ratio due to the weakness of the CH_3O radical signal with respect to the H_2CO one, and a spurious dip in the signal, marked with a blue star in the TPES.

To help assign the TPES of the CH_3O radical, the Franck–Condon factors for ionization transitions have been calculated at the M062X/aug-cc-pVTZ level of theory by using the *Gaussian* 16 program package[32] and are listed in Table II. The simulated PES is obtained by convolving the stick spectrum with a *Gaussian* function (FWHM = 40 meV), as shown in Fig. 3(b). To match the experimental TPES, the calculated Franck–Condon factor-based stick PES and the simulated PES have been energetically shifted by 64 meV from the calculated AIE (10.637 eV).

As shown in Fig. 3, the agreement between the simulated PES and the experimental TPES is satisfactory and confirms that the m/z 31-filtered and "purified" TPES corresponds to the CH_3O radical alone. Some differences between the simulated and experimental band intensities are seen for photon energies above 10.9 eV. While intensities can be affected by the presence of autoionizations, the low signal-to-noise ratio in this region precludes further comment. The absolute photon energy of the TPES has been calibrated online with the AIEs of H_2CO (10.8887 ± 0.0005 eV) and the CH_3 radical (9.838 91 ± 0.000 19 eV).[33,34] Therefore, the AIE of the CH_3O radical is determined from Fig. 3 at 10.701 ± 0.005 eV, the error bar mainly including the uncertainty of the photon energy calibration and the influences of the scanning step size and the signal-to-noise ratio.[35] The AIE agrees reasonably well with the reported values of 10.72 ± 0.01 eV[6] and 10.78 ± 0.02 eV[7] for CH_3O with HeI PES. Furthermore, the M062X/aug-cc-pVTZ calculations in this work show that the difference in zero point energy (ZPE) in the neutral and cation between CD_3O and CH_3O places the AIE of the former 28 meV above that of the latter. This puts the present AIE(CH_3O) in good agreement with the ones obtained for the deuterated species (see Table I). Note that the present result reduces the uncertainty of the literature data by a factor of 2–4. Moreover, considering the Active Thermochemical Tables (ATcT) database recommended enthalpy of formation for the neutral CH_3O radical $\Delta_fH^0{}_{0\,K}(CH_3O)$ = 28.85 ± 0.29 kJ mol^{-1},[19] the present AIE value leads to an enthalpy of formation for the CH_3O^+ cation $\Delta_fH^0{}_{0\,K}(CH_3O^+)$ = 1061.36 ± 0.41 kJ mol^{-1}.

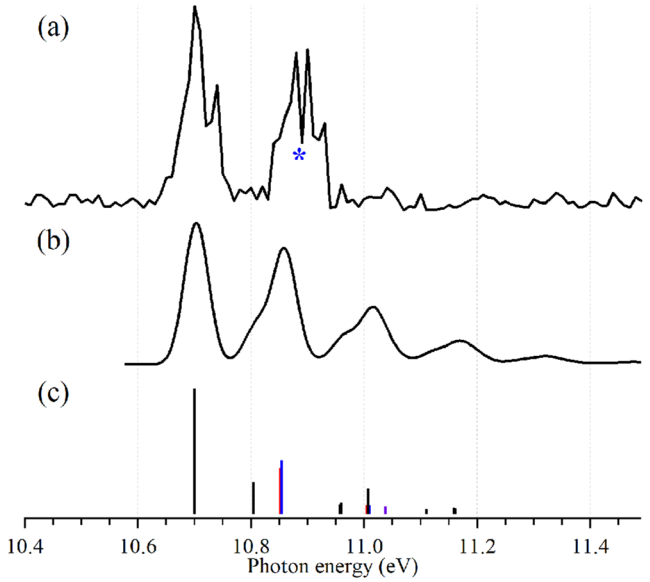

FIG. 3. (a) Experimental threshold photoelectron spectrum (TPES) of the CH_3O radical, (b) simulated PES, and (c) stick PES based upon calculated Franck–Condon factors.

TABLE II. Calculated Franck–Condon (FC) factors of the $X^2E \rightarrow X^3A_2$ ionizing transition of CH_3O.

v[a]	0^0	6^1	3^1	2^1	6^13^1	6^12^1	3^2	3^12^1	2^2	1^1	$6^13^12^1$	3^22^1	3^12^2
Energy[b]	0	840.95	1229.2	1245.2	2070.1	2086.2	2458.3	2474.4	2490.4	2724.5	3315.3	3703.5	3719.6
FC	0.320	0.082	0.117	0.135	0.026	0.030	0.023	0.065	0.024	0.021	0.013	0.016	0.015

[a] v^n corresponds to the $X^2E(v = 0) \rightarrow X^3A_2(v = n)$ ionizing transition.
[b] Calculated energies relative to the adiabatic ionization energy of CH_3O. Unit is cm^{-1}.

The C–O stretching (ν_3) and to a lesser extent the C–H stretching (ν_1) modes of CH_3O^+ are expected to be excited upon ionization.[8,9] The C–O stretching mode was observed in the HeI PES of Zhu *et al.*, and the vibrational frequency was reported at 1950 cm^{-1}.[7] The C–H stretching frequency was reported at 2469 cm^{-1} in the infrared photodissociation spectrum of the CH_3O^+–Ar complex.[36] As shown in Fig. 3, the ν_3 (C–O stretching, in red) and ν_2 (umbrella, in blue) vibrational modes of the CH_3O^+ cation are calculated to be populated upon photoionization, together with the ν_6 (H_3C–O bending) and ν_1 (C–H stretching, in purple) vibrational excitations and their combinations. The experimental signal-to-noise ratio does not allow us to refine the calculated frequencies and Franck–Condon factors, but the overall good agreement validates the theoretical methodology.

In the TPES, extra peaks can be observed at $h\nu$ = 10.740 eV and, to a lesser extent due to the lower signal, 10.930 eV, as high energy shoulders of the two vibrational bands, almost with the same spacing (~40 meV) from the main peaks. Previous theoretical calculations predicted the Jahn–Teller splitting energy of the X^2E ground state of the CH_3O radical at ~270 cm^{-1} (33 meV).[10,11] As the H_3C–O bending (ν_6) with the *e* vibrational mode is excited in the ionization process, the Jahn–Teller splitting might contribute somewhat to the two shoulder peaks, even if the limited S/N ratio precludes a detailed analysis.

IV. CONCLUSIONS

In conclusion, the VUV photoionization of the CH_3O radical has been investigated by using the state-of-the-art method of i^2PEPICO spectroscopy on the DESIRS beamline at SOLEIL. A fast flow tube combined with a microwave discharge generator was employed as a chemical reactor to initiate reactions and generate radicals. Almost all the reactants and products have been efficiently and sensitively probed in the photoionization mass spectrum to disentangle the embedded chemical reactions in the flow tube. The CH_3O radical is generated via the bimolecular reaction between CH_3 and CH_3O_2 and the self-reaction of CH_3O_2. Then, the CH_3O^+ cation from direct ionization of the CH_3O radical is successfully detected close to its ionization threshold. The mass-selected TPES of the CH_3O radical within the energy range of 9.7 eV–11.5 eV is measured after removal of the ^{13}C–isotopic formaldehyde $H_2{}^{13}CO$ signal. With the aid of the calculated Franck–Condon factors, the vibrational excitations of the CH_3O^+ cation have been assigned in the TPES and the AIE of the CH_3O radical is determined accurately at 10.701 ± 0.005 eV. The calculated ZPE difference in the neutral and cation between CD_3O and CH_3O leads to an AIE(CD_3O) of 10.729 eV. More generally, as demonstrated in this manuscript, the present work provides a benchmark and strategy to get the spectral fingerprint for very dilute and elusive species in complex atmospheric and combustion reactions.

SUPPLEMENTARY MATERIAL

See the supplementary material for possible ongoing reactions in the flow tube (Table S1) and the optimized structure of CH_3O^+ and its calculated vibrational frequencies (Fig. S1).

ACKNOWLEDGMENTS

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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