Photoionization mass spectrometric studies of the isomeric transient species CD_2OH and CD_3O

B. Ruscic and J. Berkowitz
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 6 May 1991; accepted 13 May 1991)

Both CD_2OH and CD_3O were prepared *in situ* by the reaction of F atoms with CD_3OH, and studied by photoionization mass spectrometry. The adiabatic ionization potential (I.P.) of CD_2OH was found to be 7.540 ± 0.006 eV, in good agreement with the photoelectron spectroscopy (PES) value, 7.55 ± 0.01 eV. However, the adiabatic I.P. of CD_3O was determined to be 10.726 ± 0.008 eV, in marked contrast to the PES value for CH_3O, 7.37 ± 0.03 eV, but in the expected range based on reported values of $\Delta H_f^0(CH_3O^+)$ and $\Delta H_f^0(CH_3O)$. From selected values of $\Delta H_{f0}^0(CH_2OH^+) \leqslant 172.0 \pm 0.7$ kcal/mol and $\Delta H_{f0}^0(CH_3O) = 5.9 \pm 1.0$ kcal/mol, we deduce $\Delta H_{f0}^0(CH_2OH) \leqslant -2.1 \pm 0.7$ kcal/mol and $\Delta H_{f0}^0(CH_3O^+) = 253.1 \pm 1.0$ kcal/mol.

I. INTRODUCTION

The radical species CH_3O and CH_2OH are believed to play important roles as intermediates in the combustion of hydrocarbon fuels[1,2] and in atmospheric pollution chemistry.[3,4] A high-resolution laboratory infrared spectrum of CH_2OH^+ has recently been obtained,[5] motivated in part by predictions of its presence in interstellar gas clouds. Recently, absorption spectra in the visible–UV region have been observed for both species,[6–13] primarily using laser methods (except Ref. 8). Accurate experimental vibrational frequencies are known for both species, and a rotational analysis (and hence geometric structure) is known for CH_3O. Despite this intensive study, and a wealth of information, the thermochemical data for both the neutral species and their cations are not firmly established.

Perhaps the best known of these four heats of formation is $\Delta H_f^0(CH_2OH^+)$. From the photodissociative ionization appearance potentials[14] of CH_2OH^+ (CH_3OH) and CH_2OH^+ (C_2H_5OH), one can deduce $\Delta H_{f0}^0(CH_2OH^+) \leqslant 172.0 \pm 0.7$ and $\leqslant 171.7$ kcal/mol, respectively. The selected proton affinity[15,16] (P.A.) of CH_2O at the oxygen position is given as 171.7 kcal/mol, or $\Delta H_{f298}^0 = 168$ kcal/mol. This P.A.(CH_2O) has an uncertainty[17] of at least ± 2 kcal/mol, since its value is based on P.A.(H_2O) $= 166.5 \pm 2$ kcal/mol, and hence we choose $\Delta H_{f0}^0(CH_2OH^+) \leqslant 172.0 \pm 0.7$ kcal/mol.

The heat of formation of neutral CH_2OH is less certain. The compilation of Lias *et al.*[16] selects $\Delta H_{f298}^0(CH_2OH) = -6.2 \pm 1.5$ kcal/mol, citing McMillen and Golden[18] as the source. McMillen and Golden do indeed give this value, citing Golden and Benson[19] and another reference, which has nothing to do with CH_2OH. From Golden and Benson, we find that Cruickshank and Benson[20] studied the iodination reaction

$$CH_3OH + I \rightarrow CH_2OH + HI,$$

and obtained an endothermicity of 24.6 ± 1.5 kcal/mol. Utilizing this value, Golden and Benson compute $\Delta H_{f298}^0(CH_2OH) = -4.2 \pm 1.5$ kcal/mol. However, Golden and Benson also cite Buckley and Whittle,[21] who studied the corresponding bromination reaction, and inferred an endothermicity of < 4.2 kcal/mol. From this latter observation, one can deduce $\Delta H_{f298}^0(CH_2OH) \leqslant -8.3$ kcal/mol, which is outside the error limit (-4.2 ± 1.5 kcal/mol) resulting from the iodination study. In order to give some weight to the bromination data, Golden and Benson chose $D_{298}(H - CH_2OH) = 94 \pm 2$ kcal/mol, which translates to $\Delta H_{f298}^0(CH_2OH) = -6.2 \pm 2$ kcal/mol.

Glushko *et al.*[22] select $\Delta H_{f298}^0(CH_2OH) = -4.8 \pm 2.4$ kcal/mol as the middle range of several experiments, three of which are based on an incorrect ionization potential for CH_2OH (see below). The consensus appears to be a value between -4.2 and -6.2 kcal/mol, with an uncertainty of ± 1.5 kcal/mol, or[22] $\Delta H_{f0}^0(CH_2OH) = (-2.6 \text{ to } -4.6) \pm 1.5$ kcal/mol.

For $\Delta H_f^0(CH_3O)$, most recent papers[16,23,24] cite the experiment of Batt and Milne.[25,26] These authors determined the bond energy of CH_3O–NO by kinetic measurements (assuming no activation energy) to be 41.8 kcal/mol (298 K). Using $\Delta H_{f298}^0(CH_3ONO) = -16.0$ kcal/mol from Silverwood and Thomas,[27] they obtained $\Delta H_{f298}^0(CH_3O) = 4.2 \pm 0.7$ kcal/mol. [With $\Delta H_{f298}^0(NO) = 21.82$ kcal/mol,[16] we would calculate 4.0 kcal/mol.] Subsequently, Batt and McCulloch[28] obtained $\Delta H_{f298}^0(CH_3O) = 3.8 \pm 0.2$ kcal/mol from the kinetics of dimethyl peroxide pyrolysis. Glushko *et al.*,[22] surprisingly not citing Batt and co-workers, arrive at 3.1 ± 1 kcal/mol from an examination of other sources. If we take $\Delta H_{f298}^0(CH_3O) = 4.0 \pm 1$ kcal/mol as representing the consensus of experimental data from Batt and co-workers, then[22] their $\Delta H_{f0}^0(CH_3O) = 5.9 \pm 1$ kcal/mol, while Glushko *et al.* give $\Delta H_{f0}^0(CH_3O) = 5.0 \pm 1$ kcal/mol.

At this point, it is convenient to introduce some *ab initio* calculations which have focused on the difference in stabilities of CH_2OH and CH_3O. Saebo, Radom, and Schaefer[29] show that CH_3O is 4.1 kcal/mol more stable than CH_2OH at the Hartree–Fock level (6-31** basis sets). However, when electron correlation is included, CH_2OH becomes more sta-

TABLE I. Enthalpies of formation (kcal/mol) of CH_2OH, CH_3O, and their cations, and the adiabatic ionization potentials (eV) of CH_2OH/CD_2OH and CH_3O/CD_3O. The underlined values are the currently recommended ones.

	CH_2OH	CH_3O	CH_2OH^+	CH_3O^+
ΔH^0_{f0}	$(-2.6 \text{ to } -4.6) \pm 1.5^a$ -3.1 ± 2.4^d $< \underline{-2.1 \pm 0.7^c}$	5.6 ± 0.7^b 5.0 ± 1^d $\underline{5.9 \pm 1^a}$	$< \underline{172.0 \pm 0.7^a}$	$\underline{253.2 \pm 1.0^c}$
ΔH^0_{f298}	$(-4.2 \text{ to } -6.2) \pm 1.5^a$ -6.2 ± 1.5^b -4.8 ± 2.4^d -5.8 ± 3.0^g $< \underline{-3.7 \pm 0.7^c}$	3.7 ± 0.7^b 3.1 ± 1^d $\underline{4.0 \pm 1^a}$	168^b $< \underline{170.1 \pm 0.8^a}$	$(201)^b$ 247 ± 5^e 245 ± 6^f $\underline{251.2 \pm 1.0^c}$
I.P.	$7.56 \pm 0.01^{g,h}$ 7.55 ± 0.01^g $\underline{7.540 \pm 0.006^c}$	$(8.6)^b$ 7.37 ± 0.03^g $\underline{10.726 \pm 0.008^c}$		

[a] See text for discussion of these selections. The value given for $\Delta H^0_{f298}(CH_2OH^+)$ is based on frequencies for CH_2OH^+ supplied by the authors of Ref. 31.

[b] Reference 16.

[c] Present results, for CD_2OH and CD_3O. Zero-point energy considerations (Ref. 31), Dykes's (Ref. 36) results, and unpublished data from our laboratory agree that I.P.(CH_2OH) exceeds I.P.(CD_2OH) by 0.01 eV. Similar zero-point energy calculations indicate that I.P.(CD_3O) and I.P.(CH_3O) are the same, within 0.001 eV.

[d] Reference 22.

[e] Reference 33.

[f] Reference 34.

[g] Reference 36. The value 7.55 ± 0.01 eV is for CD_2OH; 7.56 ± 0.01 eV is for CH_2OH.

[h] Reference 35.

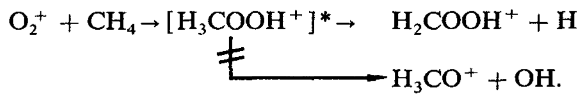
ble. At the MP3/6-31G** level, and including zero-point energies, CH_2OH is 5.0 kcal/mol more stable than CH_3O. At this level, the barrier to isomerization ($CH_3O \rightarrow CH_2OH$) is found to be 36.0 kcal/mol. Later, Colwell[30] obtained an almost identical result—CH_2OH more stable by 5.86 kcal/mol, and a barrier height of 37.29 kcal/mol—using configuration interaction (singles and doubles) with a Davidson correction and a double-zeta plus polarization basis set. However, in the recent calculation by Curtiss, Kock, and Pople[31] at the G2 level (more correlation) CH_2OH is found to be 8.8 kcal/mol more stable than CH_3O. Our prior analysis of experimental data would lead to a difference of (8.4–10.4) ± 2 kcal/mol. A previous experimental estimate of this quantity by Batt, Burrows, and Robinson[32] arrived at 7.5 kcal/mol.

Finally, we turn to $\Delta H^0_f(CH_3O^+)$. In 1984, Burgers and Holmes[33] showed that the "CH_3O^+" ions from dissociative ionization of CH_3ONO and $(CH_3)_2O$ were CH_2OH^+, by examining the collisional activation (CA) mass spectra of these product ions. Hence, earlier (lower) heats of formation of CH_3O^+ based on these measurements were invalid. They then prepared CH_3O^+ by first forming CH_3O^-, then causing it to undergo charge reversal in a collision cell. Subsequently, they obtained the CA mass spectrum of the CH_3O^+, and showed it to be clearly distinguishable from that of CH_2OH^+, demonstrating that a CH_3O^+ entity survives for $> 10^{-7}$ s. They then noted that the metastable peak from the unimolecular decomposition process

$$CD_3O^+ \rightarrow DCO^+ + D_2$$

had the same shape (i.e., the same kinetic-energy release) as that from $CD_3OD \rightarrow [D_2COD^+] \rightarrow DCO^+ + D_2$. Consequently, they argued that the transition state for formation of the DCO^+ metastable was the same, whether starting from CD_3O^+ or D_2COD^+, and that this transition state was "at or close above the enthalpy of formation of CD_3O^+." The latter conclusion was based on the "great (relative) intensity" of the metastable peak from CD_2O^+. They now obtained the appearance potential of the metastable peak from CD_3OD. Their value (15.1 ± 0.2 eV), together with literature values of $\Delta H^0_f(CD_3OD)$ and $\Delta H^0_f(D)$, leads to a heat of formation of the transition state of 247 ± 5 kcal/mol, which they equate with $\Delta H^0_f(CH_3O^+)$. In this type of experiment, no attempt is made to distinguish between ΔH^0_{f0} and ΔH^0_{f298}.

More recently, Ferguson, Roncin, and Bonazzola[34] made an estimate of $\Delta H^0_f(CH_3O^+)$ which provided some support for the value deduced by Burgers and Holmes, utilizing the following argument. They studied the reaction



$$O_2^+ + CH_4 \rightarrow [H_3COOH^+]^* \rightarrow H_2COOH^+ + H$$
$$[H_3COOH^+]^* \not\rightarrow H_3CO^+ + OH.$$

Since the reaction postulated to produce H_3CO^+ was not observed, they inferred that the O–O bond in H_3COOH^+ was stronger than the H–C bond. More quantitatively, they consider the energetics of the unobserved reaction

$$H_3COOH^+ \rightarrow H_3CO^+ + OH.$$

Utilizing a calculated value for $\Delta H_f^0(H_3COOH^+)$ of 204 kcal/mol, and an estimated value for $D(H_3CO^+–OH)$ of 50 kcal/mol, they obtain $\Delta H_f^0(H_3CO^+) = 245$ kcal/mol, with an estimated error of ± 6 kcal/mol. The various heats of formation discussed above are summarized in Table I.

The difference between the heat of formation of a neutral species and of its cation is the adiabatic ionization potential of that species, and thus the ionization potential (I.P.) provides an important tie point between these values. From our analysis of prior data (see above), we would conclude that I.P.(CH_2OH) = (7.57–7.66) ± 0.08 eV. Dyke *et al.*[35] prepared CH_2OH by the reaction of F atoms with CH_3OH, and obtained an adiabatic I.P. of 7.56 ± 0.01 eV from the photoelectron spectrum. This is close to the expected value, and could (and has been) used to infer an improved accuracy for $\Delta H_{f0}^0(CH_2OH)$. The corresponding adiabatic I.P. for CH_3O based on heats of formation is 10.5 ± 0.25 eV [if we take $\Delta H_f^0(CH_3O^+)$ from Burgers and Holmes,[33] and Ferguson *et al.*,[34] as representing ΔH_{f298}^0]. Dyke[36] has obtained a very different value, 7.37 ± 0.03 eV, for the adiabatic I.P. of CH_3O, from the products of pyrolysis of dimethyl peroxide. To the best of our knowledge, it is the only direct measurement of this ionization potential which has been reported. The major purpose of the current research was to resolve this huge discrepancy.

The reaction of F atoms with CH_3OH has been shown to produce both CH_3O and CH_2OH. McCaulley *et al.*[37] have recently studied this reaction, and review earlier results. They conclude that "the less exothermic channel, which yields CH_3O, is the major path for F + CH_3OH reaction." Dyke[36] believed that "some weak structure... in the 8.5 eV ionization energy region" was indicative of the presence of CH_3O in his photoelectron spectrum of the products of the F + CH_3OH reaction. This was purported to be more clearly visible in the products of dimethyl peroxide pyrolysis. With mass analysis, it is possible to distinguish CH_3O from CH_2OH by isotopic substitution, if rearrangement is not a major pathway. Thus, F + CD_3OH should yield CD_3O at M34, but CD_2OH at M33, which should be cleanly separable. We also have attempted to generate CH_3O by reacting H atoms with the recently synthesized[38] CH_3OF. This latter reaction should be highly exothermic, but no CH_3O^+ was observed. In addition, there was little, if any, diminution in the CH_3OF^+ intensity (indicative of reactant abundance). Earlier, unpublished studies[39] indicated that the reaction of H with HOF was also very slow.

II. EXPERIMENTAL ARRANGEMENT

The transient species CD_3O and CD_2OH were prepared *in situ* by reactions of F atoms with CD_3OH. The fluorine atoms were generated in a microwave discharge through pure F_2. The description of the flow tube and reaction cup has been given previously, as has the photoionization mass specrometric method.[40] Two samples of CD_3OH were used, one from Isotopes, Inc. (99% D atom purity) and the other from MDS Isotopes (99.9% D atom purity).

III. EXPERIMENTAL RESULTS

A. The F+CD_3OH reaction

1. CD_2OH^+, M33

The photoion yield curve of M33, presumed to be $CD_2OH^+(CD_2OH)$, is displayed in Fig. 1. At least three sloping steplike features can be observed. They correspond in energy (approximately) to the positions of the peaks in Dyke's[36] photoelectron spectrum of CD_2OH. Hence, the dominant ionization process appears to be direct ionization. The energy derivative of Fig. 1 should then approximate the photoelectron spectrum. The half-rise of the first step occurs at 1644.3 ± 1.3 Å≡7.540 ± 0.006 eV, which we take to be

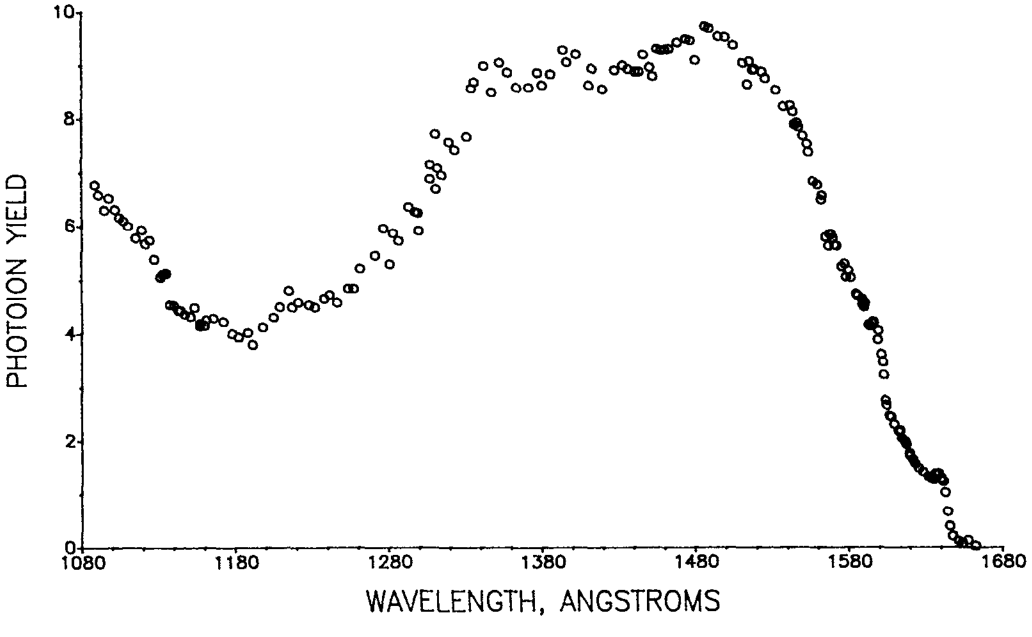


FIG. 1. The photoion yield curve of M33, presumed to be $CD_2OH^+(CD_2OH)$, where CD_2OH is a product of the F + CD_3OH reaction.

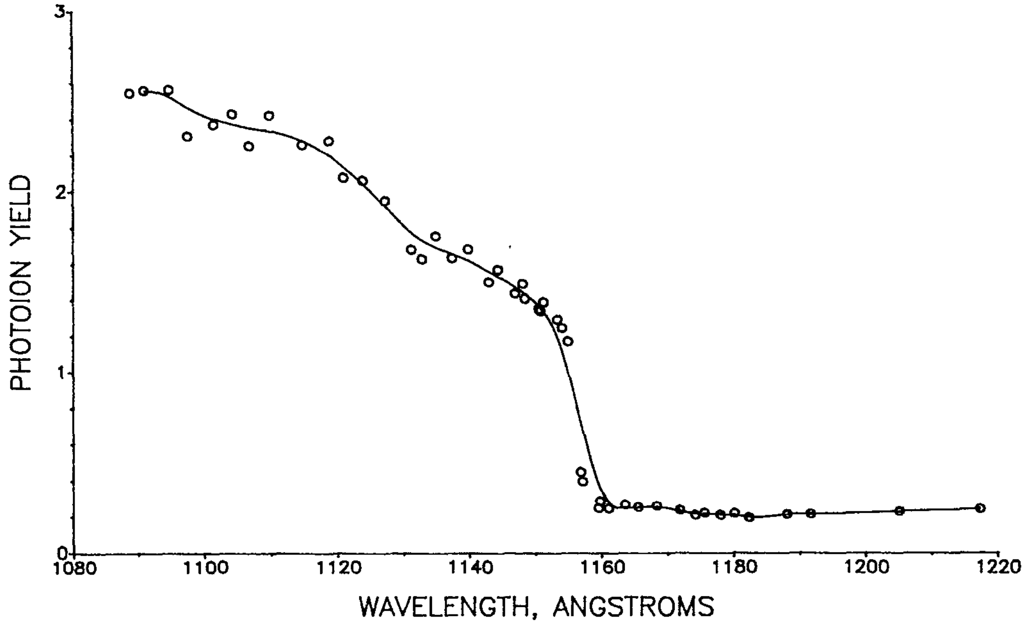


FIG. 2. The photoion yield curve of M34, presumed to be CD_3O^+ (CD_3O), where CD_3O is a product of the F + CD_3OH reaction. The smooth curve is a spline function fitted to the data points.

the adiabatic I.P. of CD_2OH. Dyke gives 7.55 ± 0.01 eV for this quantity. In Dyke's spectrum (and also in ours), there is a weak peak (background in ours) at ~7.4 eV. In order to distinguish between a still lower threshold and a hot band, we performed a simple quasidiatomic Franck–Condon calculation, assuming harmonic behavior and a frequency (presumed to be $C\text{–}O^+$) of 1610 cm^{-1}, taken from Dyke. From the relative peak intensities, we calculate a change in bond length of 0.12 Å. Whangbo, Wolfe, and Bernardi[41] have computed a contraction of 0.13 Å in the C–O bond length between CH_2OH and CH_2OH^+, in excellent agreement. Alternatively, if we assign the $0 \to 0$ peak as $0 \to 1$, we can calculate the intensity expected at the $0 \to 0$ position. The intensity of the weak peak at ~7.4 eV is about a factor 5 lower than the predicted intensity and the overall fit for higher peaks becomes much poorer. Hence, this weak feature is attributed to a hot band.

2. CD_3O, M34

The photoion yield curve of M34, presumed to be CD_3O^+ (CD_3O), is shown in Fig. 2. There is a broad underlying "background," but an abrupt increase in ion yield occurs at 1155.9 ± 0.9 Å ≡ 10.726 ± 0.008 eV. We take this to be the adiabatic I.P. of CD_3O. The underlying background has the same shape as Fig. 1, CD_2OH^+ (CD_2OH), but is about a factor 20 weaker. A possible source of this background may be the F + CD_3OH reaction itself, where some CD_2OD may be formed. Beyond threshold, one can observe sloping, steplike features with intervals of ~2400 cm^{-1}. The energy derivative of a spline fit to the data points appears in Fig. 3. If direct ionization dominates, this curve then simulates the photoelectron spectrum.

The abrupt onset can be rationalized on the basis of the available information on the structures of CH_3O and CH_3O^+, but the observed interval between peaks is more difficult to explain. Whangbo, Wolfe, and Bernardi[41] calculated C–O bond lengths of 1.428 and 1.362 Å for CH_3O and CH_3O^+, respectively, a diminution of 0.066 Å upon ionization. More recently, the structure of CH_3O has been determined experimentally. Liu *et al.*[11] reported 1.37 ± 0.02 Å for the C–O bond length, while Momose *et al.*[42] obtained 1.392 58(22) Å, both significantly smaller than calculated by Whangbo, Wolfe, and Bernardi.[41] However, a more extensive *ab initio* calculation by Curtiss, Kock, and Pople,[31] gives a C–O bond length of 1.386 Å (close to current experimental values) for CH_3O, and 1.309 Å for CH_3O^+, a diminution upon ionization of 0.076 Å. Consequently, one might expect to see a Franck–Condon vibrational progression in the C–O stretching mode of D_3CO^+/H_3CO^+. The observed stretching frequencies (cm^{-1}) for the ground-state neutral species (CH_3O:CD_3O) are 1015:1010 (Inoue, Akimoto, and Okuda[43]) and 1047:1012(?) (Foster *et al.*[10]). However, the observed interval in Figs. 2 and 3 is about 2400 cm^{-1}. The stretching frequency in CH_3O^+/CD_3O^+ can be expected to increase from that in the neutral, since r_e is calculated to decrease. We shall estimate this frequency using Badger's rule.[44] As a test, we first compute the CO stretching frequency in CH_3O/CD_3O in a quasidiatomic picture, i.e., $\mu = 7.742/8.626$ amu and $r_e = 1.386$ Å, and obtain $\omega = 1076/1019$ cm^{-1}, somewhat higher than the experimental values. The corresponding calculation for CH_3O^+/ CD_3O^+ gives $\omega = 1279/1212$ cm^{-1}. Thus, the C–O stretching frequency in CD_3O^+ is predicted to be ~1200 cm^{-1}, about half the observed interval. This normal mode is totally symmetric, and hence is expected to appear in single, not double, quanta intervals. The large discrepancy suggests mixing with another a_1 mode, or conceivably a Fermi resonance. An obvious candidate is the C–H/C–D stretch, for which Jackels[45] has calculated 3118/2237 cm^{-1}. Mixing was also invoked by Dyke[36] to explain the anomalous behav-

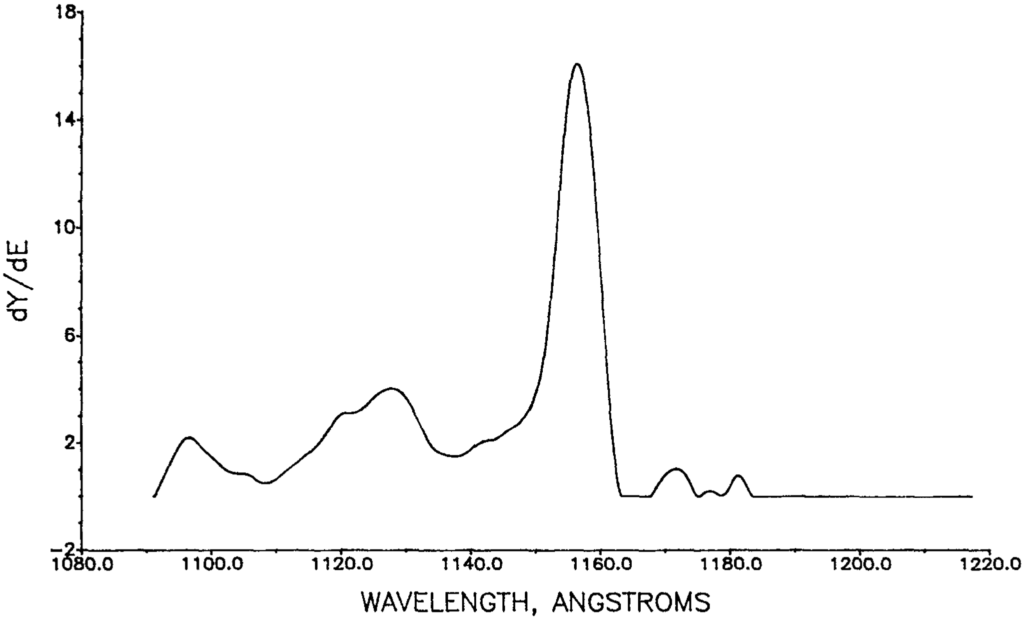


FIG. 3. The energy derivative of the spline function in Fig. 2, which is intended to simulate a photoelectron spectrum.

ior of the CO stretching mode in the photoelectron spectra of CH_2OH/CD_2OH, where the deuterated species had a measured interval of 1810 ± 30 cm^{-1}, while for the protonated species it was 1650 ± 30 cm^{-1}.

In summary, a quasidiatomic picture cannot explain the 2400 cm^{-1} interval in the spectrum of CD_3O^+. A more-involved normal-coordinate analysis may shed some light on this behavior, but the abrupt onset, favoring the 0–0 transition, is a plausible inference from the calculated geometric structures of CH_3O and CH_3O^+.

IV. DISCUSSION OF RESULTS

A. CH_2OH–CH_2OH^+

In Sec. I (Introduction), we concluded that $\Delta H^0_{f0}(CH_2OH^+)$ was known to better accuracy than $\Delta H^0_{f0}(CH_3O)$, but that their difference should be (7.57–7.66) $\pm$ 0.08 eV. Both the photoelectron spectroscopic value[35,36] (7.56 ± 0.01 eV) and the current photoionization value for CD_2OH, 7.540 ± 0.006 eV, fall slightly below these bounds. Taking $\Delta H^0_{f0}(CH_2OH^+) \leqslant 172.0 \pm 0.7$ kcal/mol, and adding 0.01 eV to the presently determined I.P. for CD_2OH, to convert it to I.P.(CH_2OH), we can deduce $\Delta H^0_{f0}(CH_2OH) \leqslant -2.1 \pm 0.7$ kcal/mol [or $\Delta H^0_{f298}(CH_2OH) \leqslant -3.7 \pm 0.7$ kcal/mol], which is at the upper end of the range given in Sec. I.

B. CH_3O–CH_3O^+

The situation regarding CH_3O and CH_3O^+ is far more controversial. From the difference in these heats of formation given in Sec. I, we predicted an adiabatic I.P. of 10.5 ± 0.25 eV, whereas Dyke[36] reported 7.37 ± 0.03 eV. Our measured value for CD_3O is 10.726 ± 0.008 eV. Since we had concluded that $\Delta H^0_{f0}(CH_3O) = 5.8 \pm 1$ kcal/mol was known to better accuracy than its cation, we can now infer that $\Delta H^0_{f0}(CH_3O^+) = 253.1 \pm 1.0$ kcal/mol. We can also estimate $\Delta H^0_{f298}(CH_3O^+) = 251.2 \pm 1.0$ kcal/mol, which if applicable, is at the upper end of the experimental determinations of Burgers and Holmes[33] (247 ± 5 kcal/mol) and Ferguson, Roncin, and Bonazzola[34] (245 ± 6 kcal/mol).

The *ab initio* calculations of Bouma, Nobes, and Radom[46] have been cited by Burgers and Holmes, and Ferguson, Roncin, and Bonazzola as yielding $\Delta H^0_f(CH_3O^+) = 260$ kcal/mol. This value is not given explicitly by Bouma, Nobes, and Radom. They state that $\Delta H^0_f(CH_3O^+)$ exceeds $\Delta H^0_f(CH_2OH^+)$ by 387 kJ/mol$\equiv$92.5 kcal/mol, and they make passing reference to an experimental value of $\Delta H^0_f(CH_2OH^+) = 707$ kJ/mol$\equiv$169 kcal/mol, from which one can deduce $\Delta H^0_f(CH_2O^+) = 261.5$ kcal/mol. Alternatively, they calculate that the reaction

$$CH_3OCH_3^+ \rightarrow CH_2OH^+ + CH_3$$

is endothermic by 36 kJ/mol$\equiv$8.6 kcal/mol. By taking $\Delta H^0_{f0}(CH_3OCH_3^+) = 191.5$ kcal/mol and $\Delta H^0_{f0}(CH_3) = 35.6$ kcal/mol from Lias *et al.*,[16] we obtain $\Delta H^0_{f0}(CH_2OH^+) = 164.5$ kcal/mol (significantly *lower* than our recommended value, $\leqslant 172.0 \pm 0.7$ kcal/mol) and hence $\Delta H^0_{f0}(CH_3O^+) = 257.0$ kcal/mol, still about 4 kcal/mol *higher* than our deduced value.

The photoelectron spectrum attributed to CH_3O by Dyke requires further discussion. In Sec. I we noted that Batt and McCulloch[28] obtained a reasonable value for $\Delta H^0_f(CH_3O)$ from the pyrolysis of dimethyl peroxide. Hence, it is plausible to assume (as Dyke evidently did) that pyrolysis of dimethyl peroxide should yield CH_3O radicals. However, his photoelectron spectrum looks roughly like a blurred CH_2OH spectrum. Perhaps some of the CH_3O radicals have relaxed to the more-stable CH_2OH isomer before leaving the pyrolysis cell. His spectrum ends at an energy < 9.5 eV, in both the F + CD_3OH reaction and the pyrolysis of dimethyl peroxide. Hence, we are not privy to the region around 10.7–10.8 eV, where our results show that CH_3O^+/CD_3O^+ should appear. Even the $F + CH_3OH$ results are not shown beyond ~10.0 eV. He would probably have had difficulty in the $F + CH_3OH/CD_3OH$ experiments, since I.P.(CH_3OH) = 10.85 eV.[16] This reactant species would very likely contribute a large peak to the photoelectron spectrum, and could overwhelm a small peak at ~10.73 eV. Dimethyl peroxide has a rich photoelectron spectrum,[47] beginning at ~9.1 eV. It may have been difficult to identify a small peak within this spectrum.

Finally, we should like to pose the possibility that CD_3O^+ may actually be formed from CD_3OH. In earlier work, one of us[48] examined the photoion yield curves of M34 (assumed to be CD_3O^+) and M33 (assumed to be CD_2OH^+) from CD_3OH. The abundance of M34 was about 1/10 that of M33. Both ions had about the same appearance potential, but M34 displayed a significant increase in intensity between ~14.5 and 16 eV which M33 did not. The derivatives of these curves (Fig. 6 in Ref. 48) emphasized these differences, showing that M34 had a much larger contribution in the vicinity of the second excited state of CD_3OH^+ than did M33. With the currently deduced $\Delta H^0_{f0}(CD_3O^+)$, the appearance potential of CD_3O^+ from CD_3OH is 15.2 eV. Hence, a significant portion of the second excited state of CD_3OH could decompose into $CD_3O^+ + H$. [The M34 signal at lower energy presumably arises from rearrangement in the decomposition process, giving $CD_2OD^+ + H$. The amount of CD_3OD impurity (ca. 1%) is too small to account for the M34 intensity at lower energy.] The calculation of Bouma, Nobes, and Radom[46] indicates that the CH_3O^+, and therefore CD_3O^+, is a triplet. It could have difficulty decomposing into $DCO^+ + D_2$, which represents a singlet surface. Burgers and Holmes find that CD_3O^+ from charge reversal gives rise to a metastable peak (DCO^+) which is virtually identical to that obtained by electron impact on CD_3OH at 15.1 eV. This could be CD_3O^+ being formed, instead of the transition state postulated by these authors. Dill, Fischer, and McLafferty[49] have performed collisional activation studies on COH_3^+ ions from CH_3OH at 20 and 70 eV, and find no difference. Hence, they attribute all of these ions to the CH_2OH^+ structure. However, a mixture of CH_3O^+ and CH_2OH^+, with a small contribution of CH_3O, may have escaped detection. Burgers and Holmes have generated a "pure" CD_3O^+ collisional activation spectrum, and show how it differs from the CA spectrum of COD_3^+ from dissociative ionization of deuteromethanol, but again, it seems possible that a mixture of the two could conceivably be present.

The lifetime of $^3[CD_3O^+]$ comes into question here. Burgers and Holmes find that "some 20% of the initially formed $^3[D_3CO]^+$ ions" undergo unimolecular dissociation in the μs timeframe. Although they do not specify this time more precisely, the acceleration voltages in a magnetic mass spectrometer are typically 4–8 kV, whereas those in our quadrupole mass spectrometric apparatus are ~25 V. Hence, their flight time in the field free region where unimolecular dissociation occurs is of order 1 μs, certainly less than 10 μs, whereas our flight times are several tens of μs. Hence, we would expect to lose many more CD_3O^+ ions. In fact, our CD_3O^+ intensity is, within a factor ~3, about as intense as CD_2OH^+. The expectation from the kinetics experiments[37] is that CD_3O and CD_2OH are formed in comparable amounts, and their photoionization cross sections also should be comparable. Our inference is that CD_3O^+ in its $v' = 0$ state probably has a longer lifetime. Burgers and Holmes are forming their CD_3O^+ by charge reversal from CD_3O^-, which could give rise to CD_3O^+ with more average vibrational energy, and hence a shorter lifetime.

CD_3O is one of the rare molecules whose adiabatic ionization potential (10.726 ± 0.008 eV) is higher than the calculated appearance potential of its fragments [$DCO^+ + H_2$, 8.30 eV (Ref. 16)]. Other examples include HNO_3 (Ref. 16) [I.P. = 11.95 eV, A.P.($NO^+ + HO_2$) = 11.64 eV] and the recently studied CH_3OF.[50]

Note added to proof. After the completion of this work, we examined the photoionization spectra of CD_3O and CH_3O, generated by reacting F atoms with CH_3OH, CH_3OD, and CD_3OD. Although CD_3O^+ was observed, CH_3O^+ was not. Instead, the HCO^+ decomposition product was detected, indicating that CH_3O^+ has a significantly shorter lifetime than CD_3O^+. A complete account of these studies is being prepared for publication.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

[1] *Oxidation of Organic Compounds*, Vols. I–III in Advances in Chemistry Series (American Chemical Society, Washington, D.C., 1968).

[2] K. L. Demerjian, J. A. Kerr, and J. G. Calvert, Adv. Environ. Sci. Technol. **4**, 1 (1974).

[3] J. Heicklen, *Atmospheric Chemistry* (Academic, New York, 1976).

[4] *Chemical Kinetic Data Needs for Modeling the Lower Troposphere*, Natl. Bur. Stand. (U.S.) Spec. Publ. 557, edited by J. T. Herron, R. E. Huie, and J. A. Hodgeson (U.S. GPO, Washington, D.C., 1979).

[5] T. Amano and H. E. Warner, Astrophys. J. **342**, L99 (1989).

[6] C. S. Dulcey and J. W. Hudgens, J. Chem. Phys. **84**, 5262 (1986).

[7] D. S. Bomse, S. Dougal, and R. L. Woodin, J. Phys. Chem. **90**, 2640 (1986).

[8] P. Pagsberg, J. Munk, A. Sillesen, and C. Anastasi, Chem. Phys. Lett. **146**, 375 (1988).

[9] G. R. Long, R. D. Johnson, and J. W. Hudgens, J. Phys. Chem. **90**, 4901 (1986).

[10] S. C. Foster, P. Misra, Y-T. D. Lin, C. P. Damo, C. C. Carter, and T. A. Miller, J. Phys. Chem. **92**, 5914 (1988).

[11] X. Liu, C. P. Damo, T-Y. D. Lin, S. C. Foster, P. Misra, L. Yu, and T. A. Miller, J. Phys. Chem. **93**, 2266 (1989).

[12] J. Kappert and F. Tanys, Chem. Phys. **132**, 197 (1989).

[13] A. Geers, J. Kappert, F. Temps, and J. W. Wiebrecht, J. Chem. Phys. **93**, 1472 (1990).

[14] K. M. A. Refaey and W. A. Chupka, J. Chem. Phys. **48**, 5205 (1968).

[15] S. G. Lias, J. F. Liebman, and R. D. Levin, J. Phys. Chem. Ref. Data **13**, 695 (1984).

[16] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, Suppl. 1 (1988).

[17] Lias *et al.* (Ref. 15, p. 701) obtain P.A.(CH_2O) = 171.7 kcal/mol by taking ΔP.A.(CH_2O–H_2O) = 5.2 kcal/mol from K. Tanaka, G. I. Mackay, and D. Bohme, Can. J. Chem. **56**, 193 (1978), and their standard, P.A.(H_2O) = 166.5 ± 2 kcal/mol. However, Tanaka, Mackay, and Bohme actually give 4.5 kcal/mol for ΔP.A. Furthermore, Tanaka,

Mackay, and Bohme prefer P.A.(CH_2O) as a standard, based on the appearance potential of CH_2OH^+ from CH_3OH already discussed (Ref. 14). Additional confusion is introduced for $\Delta H_f^0(CH_2OH^+)$, since Tanaka, Mackay, and Bohme appear to use the thermal electron convention, while Lias *et al.* (Ref. 16) use the stationary electron convention. If one takes $\Delta H^0_{f298}(CH_2O) = -26.0$ kcal/mol and $\Delta H^0_{f298}(H^+) = 365.7$ kcal/mol from Ref. 16, one obtains P.A.(CH_2O) = 169.5 or 169.4 kcal/mol. Tanaka, Mackay, and Bohme appear to have combined a stationary electron convention value for $\Delta H^0_{f298}(CH_2OH^+)$ with a thermal electron convention value for $\Delta H^0_{f298}(H^+) = 367.2$ kcal/mol to obtain P.A.(CH_2O) = 170.9 ± 1.2 kcal/mol.

[18] D. F. McMillen and D. M. Golden, Annu. Rev. Phys. Chem. **33**, 493 (1982).

[19] D. M. Golden and S. W. Benson, Chem. Rev. **69**, 125 (1969).

[20] F. R. Cruickshank and S. W. Benson, J. Phys. Chem. **73**, 733 (1969).

[21] E. Buckley and E. Whittle, Trans. Faraday Soc. **58**, 536 (1962).

[22] V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veitz, V. A. Medredev, G. A. Khachkuruzov, and V. C. Yungman, *Termodinamicheskie Cvoistva Individual'nikh Veshchestv* (Nauka, Moscow, 1978 and 1979), Vols. 1 and 2.

[23] M. Nonella and J. R. Huber, Chem. Phys. Lett. **131**, 376 (1986).

[24] O. Benoist D'Azy, F. Lahmani, C. Lardeux, and D. Solgadi, Chem. Phys. **94**, 247 (1985).

[25] L. Batt, K. Christie, R. T. Milne, and A. J. Summers, Int. J. Chem. Kinet. **6**, 877 (1974).

[26] L. D. Batt and R. T. Milne, Int. J. Chem. Kinet. **6**, 945 (1974).

[27] R. Silverwood and J. H. Thomas, Trans. Faraday Soc. **63**, 2476 (1967).

[28] L. Batt and R. D. McCulloch, Int. J. Chem. Kinet. **8**, 491 (1976).

[29] S. Saebø, L. Radom, and H. F. Schaefer III, J. Chem. Phys. **78**, 845 (1983).

[30] S. M. Colwell, Theor. Chim. Acta **74**, 123 (1988).

[31] L. A. Curtiss, D. Kock, and J. A. Pople, J. Chem. Phys. **95**, 4040 (1991).

[32] L. Batt, J. P. Burrows, and G. N. Robinson, Chem. Phys. Lett. **78**, 467 (1981).

[33] P. C. Burgers and J. L. Holmes, Org. Mass Spectrom. **19**, 452 (1984).

[34] E. E. Ferguson, J. Roncin, and L. Bonazzola, Int. J. Mass Spectrom. Ion Proc. **79**, 215 (1987).

[35] J. M. Dyke, A. R. Ellis, N. Jonathan, N. Keddar, and A. Morris, Chem. Phys. Lett. **111**, 207 (1984).

[36] J. M. Dyke, J. Chem. Soc. Faraday Trans. 2 **83**, 69 (1987).

[37] J. A. McCaulley, N. Kelly, M. F. Golde, and F. Kaufman, J. Phys. Chem. **93**, 1014 (1989).

[38] M. Kol, S. Rozen, and E. Appelman, J. Am. Chem. Soc. (submitted).

[39] E. H. Appelman (private communication).

[40] S. T. Gibson, J. P. Greene, and J. Berkowitz, J. Chem. Phys. **83**, 4319 (1985); J. Berkowitz, J. P. Greene, H. Cho, and B. Ruscic, *ibid.* **86**, 1235 (1987).

[41] M.-H. Whangbo, S. Wolfe, and F. Bernardi, Can. J. Chem. **53**, 3040 (1975).

[42] T. Momosa, Yu. Endo, E. Hirota, and T. Shida, J. Chem. Phys. **88**, 5338 (1988).

[43] G. Inoue, H. Akimoto, and M. Okuda, J. Chem. Phys. **72**, 1769 (1980).

[44] G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, NJ, 1950), p. 457.

[45] C. F. Jackels, J. Chem. Phys. **76**, 505 (1982).

[46] W. J. Bouma, R. H. Nobes, and L. Radom, Org. Mass Spectrom. **17**, 315 (1982).

[47] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules* (Japan Scientific Societies, Tokyo and Halsted, New York, 1981), p. 141.

[48] J. Berkowitz, J. Chem. Phys. **69**, 3044 (1978).

[49] J. D. Dill, C. L. Fischer, and F. W. McLafferty, J. Am. Chem. Soc. **101**, 6531 (1979).

[50] B. Ruscic, E. Appelman, and J. Berkowitz, J. Chem. Phys. (submitted).