

Laser photodetachment electron spectrometry of methoxide, deuteromethoxide, and thiomethoxide: Electron affinities and vibrational structure of CH₃O, CD₃O, and CH₃S

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Photodetachment of the three anions CH₃O⁻, CD₃O⁻, and CH₃S⁻ by a fixed-frequency argon ion laser at 488 nm and subsequent energy analysis of the photoelectrons yields the photoelectron spectra of these species. From the spectra, electron affinities were determined: E.A.(CH₃O) = (1.570 ± 0.022) eV, E.A.(CD₃O) = (1.552 ± 0.022) eV, E.A.(CH₃S) = (1.882 ± 0.024) eV. From the vibrational structure appearing in the spectra, and the shifts observed upon deuteration, the predominant motion excited in the neutral upon photodetachment of CH₃O⁻ and CD₃O⁻ is found to be the symmetric hydrogen umbrella bend at 1325 ± 30 and 1010 ± 30 cm⁻¹, respectively. In CH₃S both the symmetric hydrogen bend and the carbon-sulfur bond stretch (680 ± 40 cm⁻¹) are excited. From the observed hot bands, some vibrational frequencies of the negative ions are also derived.

I. INTRODUCTION

Both the alkoxide ion (RO⁻) and the alkoxy radical (RÖ) are ubiquitous organic species. Alkoxide ions are often used to catalyze base-sensitive reactions, while alkoxy radicals are often used to initiate radical reactions. Alkoxy radicals can be found in the decomposition of peroxides, radiolysis of alcohols, flames, and have even been postulated to exist in interstellar molecular "clouds." The simplest of these species is methoxy (CH₃O) and its corresponding negative ion, methoxide (CH₃O⁻).

The structure of these two species is understood to be C_{3v}, with the hydrogens bound symmetrically to the central carbon atom. *Ab initio* calculations^{1,2} have been performed and the predicted geometries are summarized in Table I. For the methoxy radical, spin-orbit and Jahn-Teller effects can occur which should significantly affect the radical's structure.

The technique of laser photoelectron spectrometry of negative ions³ provides electron affinities and some vibrational frequencies for both the ion and the resulting neutral species. In the methoxy radical it will be shown that the vibration predominately excited upon photodetachment is the symmetric hydrogen bend, the "umbrella" mode. The frequencies for this motion are obtained, as are the Franck-Condon factors for the geometry change accompanying photodetachment, indicative of the relative difference for the geometries of the ion and the neutral radical.

Photodetachment of methoxide anion (CH₃O⁻) has previously been studied in the gas phase.⁴ These studies, making use of ions trapped in an ion cyclotron resonance trap and a tunable photon source, examined the disappearance of trapped methoxide ions as a function of photon wavelength. The electron affinity (E.A.) of the methoxy radical was assigned to the photon energy corresponding to the threshold for this process, 1.59 ± 0.04

eV. The gross behavior of the cross section, an almost linear increase from threshold as the light was tuned to shorter wavelengths, was superimposed upon small variations resulting from the individual thresholds for various vibrational or rotational energies left in the states of the neutral product. In addition to the individual thresholds for leaving the product with internal energy, internal energy from an unknown fraction of rotationally and vibrationally excited negative ions trapped along with ions closer to their ground states was available to the detachment and could possibly have produced an artificially low threshold for the detachment. This hot-band threshold problem makes the otherwise simple program of discovering the electron affinity from the photodetachment threshold more or less uncertain,⁵ although this method of determining electron affinities is in principle exact and can be extremely accurate when not beset by these hot-band issues.⁶ In part to shed light on how serious this hot-band issue is, we have determined the electron affinity by photoelectron spectrometry, comparing it with the photodetachment threshold measurements.

Finally, in the discussion of this radical we will comment on the heat of formation of methoxy.⁷⁻⁹ A thermodynamic cycle formed by the neutral CH₃O-H bond strength, the proton affinity of CH₃O⁻ and the electron affinity of CH₃O• (plus the ionization potential of H) is inconsistent, and we will point out how this situation can be improved.

Because of the close structural similarity of the methoxy radical to both the deuterium and sulfur substituted species (CD₃O and CH₃S) these have also been

TABLE I. Calculated geometries of methoxy and methoxide.

State	r(CH), Å	r(CO), Å	HCO, degrees	
CH ₃ O \tilde{X}^2E	1.08	1.44	109	(Ref. 1)
CH ₃ O ⁻ \tilde{X}^1A_1	1.12	1.39	114	(Ref. 1)
CH ₃ O ⁻ \tilde{X}^1A_1	1.11	1.41	115	(Ref. 2)

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studied by photoelectron spectrometry of their negative ions and are reported here.

II. EXPERIMENTAL

The apparatus for the laser photoelectron spectrometry of negative ions is detailed elsewhere.³ Briefly, negative ions, extracted from an electrical discharge, are formed into a mass-selected beam. This beam crosses an intense laser flux at the inlet of a hemispherical electron energy analyzer. Photodetached electrons that pass through the analyzer are counted; as the analyzer energy is swept out, a spectrum of electron counts vs kinetic energy is formed.

The argon ion laser used in these experiments operates with the detachment region intracavity, lasing on the 488 nm line unless specifically noted otherwise. The ions are generated in an electrical discharge typically at pressures of 0.2 torr. For CH₃O⁻ either a mixture of CH₃OH/N₂O or CH₃OH alone is used, while the totally deuterated alcohol produced CD₃O⁻. CH₃O⁻ can also be generated from dimethyl oxalate. The thio compound CH₃SCH₃ produced the anion CH₃S⁻. Production of ions with CH₃OD confirmed the methoxide structure for the ion: very little mass 32 (mostly O₂⁻ as identified by photoelectron spectrometry) was formed in comparison to the relatively large amounts of mass 31 extracted from the source.

The electron analyzer is calibrated in two ways. First, the electron energy scale nonlinearity is determined by measuring the peak separations for NH⁻ photodetachment and comparing these with the known energy separation obtained from optical spectroscopy.¹⁰ Second, the detachment of a reference ion establishes the absolute energy scale. For methoxide and deuteromethoxide the reference used was O⁻ (effective E.A. = 1.465 ± 0.005 eV)^{6,11} and for thiomethoxide the reference ion was SH⁻ (effective E.A. = 2.324 ± 0.005 eV when averaged over spin-orbit components^{12,13}). The electron kinetic energy in the center-of-mass reference frame is given by³

$$\text{K. E.} = \left[2.540 \text{ eV} - \text{E. A.}_{\text{ref}} - \gamma\Omega_{\text{ref}} - \frac{mW}{M_{\text{ref}}} \right] + \gamma\Omega_x + \frac{mW}{M_x}$$

The term in the brackets expresses the zero electron energy offset; it would go to zero if Ω , the laboratory energy measurement, needed no calibration correction. In this expression 2.540 eV is the laser photon energy, E.A._{ref} is the effective electron affinity of the reference ion (O⁻ or SH⁻), γ is the scale compression correction,³ and Ω_x and Ω_{ref} are the laboratory potentials of the electrons from species x being measured and the center of the reference peak, respectively. The last term contains the center-of-mass corrections, m being the electron mass, M_x and M_{ref} being the masses of the species x and the reference, and W being the beam energy; this term corrects for the slight backward scattering in the center of mass frame in order for the electrons to enter the energy analyzer at 90° to the beam path. The electron analyzer has an energy resolution of approximately 60 meV (FWHM). Peak centers can be located to ± 5 meV.

The intensity of the photoelectrons at a given electron energy E depends upon the angle θ between the electric vector of the light and the electron collection direction according to¹⁴

$$I(\theta) = \frac{\sigma}{4\pi} [1 + \beta(E)P_2(\cos \theta)],$$

where σ is the average photodetachment cross section, β is the anisotropy parameter, and P_2 is the second Legendre polynomial. The spectra in this paper were obtained with θ such that $P_2(\cos \theta)$ was zero, and hence they represent total relative photodetachment cross sections.

III. RESULTS

The photoelectron spectrum taken at low resolution (20 meV per data point) of the mass 31 ion is shown in Fig. 1. This ion was formed from CH₃OD, yet the spectrum is identical with that of the ion formed from the regular alcohol CH₃OH, indicating that the ion structure is methoxide (CH₃O⁻) rather than hydroxymethide (CH₂OH⁻). This alkoxide structure of the ion agrees with our expectations, since the electron affinity of hydroxyl is much greater than methyl, and energetics would favor the binding of the excess electron to the oxygen rather than the carbon. In fact, no evidence could be found for the CH₂OH⁻ ion, although a low E.A. species was formed in discharges of CH₃OH/N₂O. However, this low E.A. species of mass 31 is presumably HNO⁻: The vibrational spacings in the photoelectron spectrum agree with what is known about HNO; it is formed only when nitrogen was present in the source; and it has also been observed in the preparation of methoxide from methyl nitrite in ICR experiments.¹⁵

Higher resolution spectra (5 meV per point) reveal the energy spacings of the vibrations produced in the neutral CH₃O (Fig. 2) and CD₃O (Fig. 3) by the photodetachment process. The vibrations that are expected to be allowed are the three A₁ symmetric modes: the C–O stretch ν_3 , the symmetric C–H stretch, ν_1 , and the C–H “umbrella” bend ν_2 . The reduction of vibra-

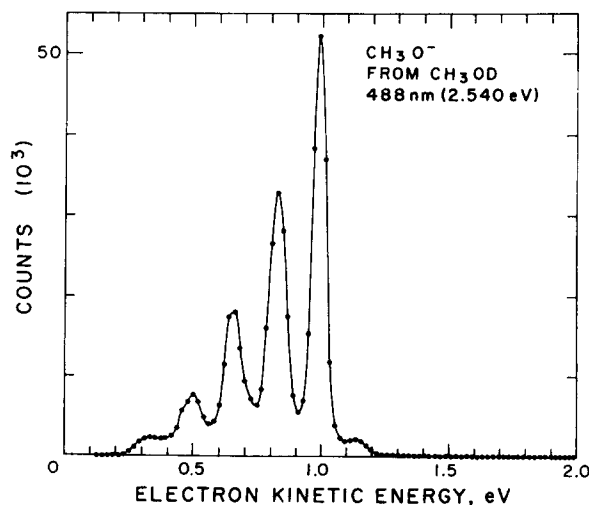


FIG. 1. Photoelectron spectrum of methoxide anion. Approximately 20 meV per point.

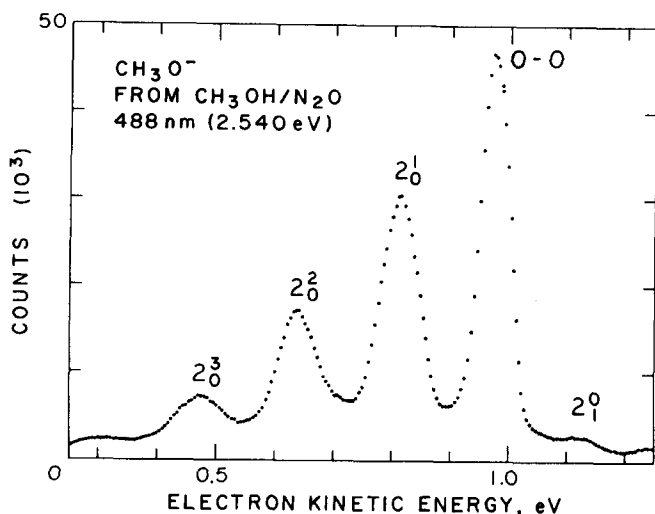


FIG. 2. Photoelectron spectrum of methoxide, approximately 5 meV per point.

tional spacings upon deuteration indicates the progression results from a hydrogen motion, and the energy spacing (around 1300 cm^{-1} for CH_3O) is more characteristic of a hydrogen bend rather than stretch. Table II summarizes the vibrational information obtained from photodetachment.

The thiomethoxide spectrum is qualitatively different from the methoxide spectrum, as shown in Fig. 4. A strong O-O forms, with a small set of vibrations to the low energy side indicative of the vibrations of the neutral product. The features of this spectrum are summarized in Table III.

An electron affinity proper is the energy difference between the lowest respective rotational, vibrational, and spin-orbit levels of the ion and the neutral. However, in the photoelectron spectrum an envelope of transitions between the individual rotational, vibrational, and spin-orbit levels of the ion and neutral is actually observed, originating from the roughly thermal distribution of ions in these levels. Thus an "electron af-

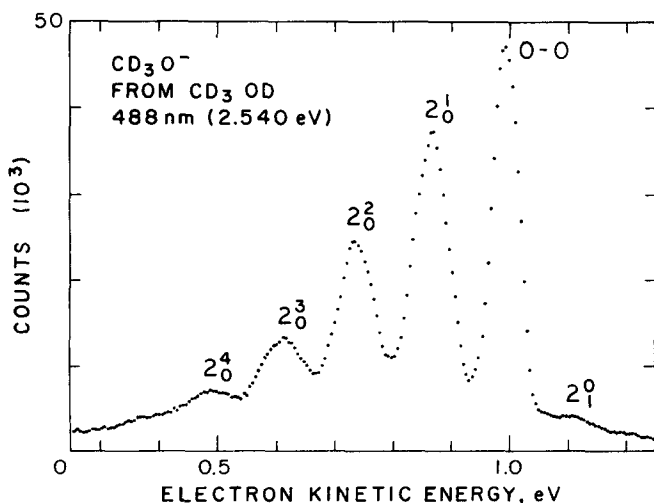


FIG. 3. Photoelectron spectrum of deuteromethoxide at 5 meV per data point.

TABLE II. Methoxide photodetachment peaks.

Assignment	Energy(eV)	Intensity(%)	Difference(cm^{-1})
CH_3O^- 2_1^0	1.104	(6) ^b	...
			1075(100) ^a
CH_3O 0-0	0.971	39	...
			1310(40)
2_0^1	0.809	29	...
			1420(60)
2_0^2	0.633	19	...
			1310(60)
2_0^3	0.470	8	...
			1270(100)
2_0^4	0.313	5	...
CD_3O^- 2_1^0	1.101	(4) ^b	...
			915(100) ^a
CD_3O 0-0	0.988	32	...
			1025(40)
2_0^1	0.861	32	...
			1035(50)
2_0^2	0.733	21	...
			1020(70)
2_0^3	0.606	11	...
			965(80)
2_0^4	0.487	4	...

^aUncertainty in the last digits in parentheses.

^bRelative to 100% in the 0-0.

finity" derived from the center of the 0-0 photoelectron peak may differ from the electron affinity proper. Corrections for this effect have been described for diatomic molecules,³ and can be extended to nonlinear polyatomic molecules. Usually, the approximation can be made that the energies of rotation, vibration, and spin-orbit are separable, and therefore the problem breaks down into these three separate categories. The "raw" electron affinities derived from the positions of the photoelectron peaks are presented in Table IV, along with the calculated corrections to these electron affinities.

The vibrational correction accounts for the shift in the photoelectron peak by sequence bands. Because vi-

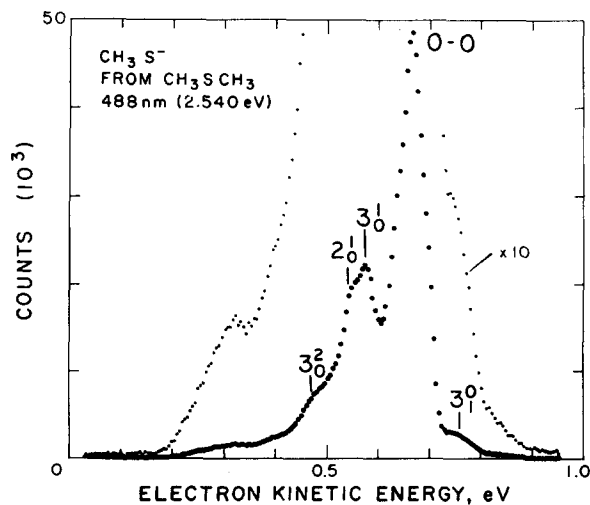


FIG. 4. Photoelectron spectrum of thiomethoxide at 5 meV per point.

TABLE III. CH₃S photodetachment peaks.

Assignment	Energy(eV)	Intensity(%)	Position(cm ⁻¹)
CH ₃ S ⁻ 3 ₁ ⁰	0.723	(10) ^b	-625(80) ^a
CH ₃ S 0-0	0.646	57	0
3 ₀ ¹	0.562	21	680(60)
2 ₀ ¹	0.517	14	1040(80)
3 ₀ ²	0.466	7	1450(80)

^aUncertainty in the last digits in parentheses.^bRelative to 100% in the 0-0.

brational frequencies are very similar in the ion and the neutral, the 0-0 peak is contaminated by other transitions that do not change their vibrational quantum numbers and originate from vibrationally excited states of the ion. Because the vibrational frequencies do change a bit, these sequence bands do not lie directly over the 0-0 peak, but cluster around it. By knowing the frequencies of the ion and neutral, and by knowing the populations of the vibrational levels of the ion, these sequence band contributions can be estimated and corrected for. In this case very few frequencies were known, but those not directly measured could be estimated from the isoelectronic chlorinated or fluorinated methanes. These frequencies were then assumed to vary no more than 10% on the average upon detachment. A vibrational temperature of 1000 ± 500 K was assumed to characterize the populations of the ion vibrational levels.

The rotational corrections were calculated from an approximation for the difference in the centroids of the neutral and ion rotational energy distributions. For a symmetric top, neglecting nuclear statistics, the correction to the E. A. is¹⁶

$$(B'' - B')(kT/B'' + 1/4) + [(B'' - A'') - (B' - A')]kT/(B'' - A''),$$

valid for transitions that approximately preserve rotational quantum numbers J and K and for kT much larger than B'' or $(B'' - A'')$. The rotational constants (B'' , A'' of the ion; B' , A' of the neutral) were estimated, principally from the calculations of Yarkony *et al.*¹ for methoxide, but for thiomethoxide, it was assumed that constants resembling those of CH₃Cl would have at most 5% variations on detachment. In this instance T was assumed to be 1000 ± 500 K.

The spin-orbit correction for methoxy E. A. is more difficult to estimate. The size of the spin-orbit splitting could be¹⁷ as high as 100 cm⁻¹, while we have chosen a value of 70 ± 30 cm⁻¹. The reasoning for this is that methoxy should act much like hydroxyl with the exception of the quenching effect of the CH₃. The highest spin-orbit constant that could then appear would be the 139 cm⁻¹ of the unquenched hydroxyl¹⁸; half of this is 70 cm⁻¹. Thus our estimate is little more than a guess.

For the thio compound a spin-orbit splitting of 200 cm⁻¹ was estimated on the same basis as the CH₃O split-

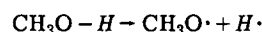
ting. A spin orbit splitting slightly larger than this may have been observed in an ICR photodisappearance experiment.¹⁹

IV. DISCUSSION

A. Electron affinity and heat of formation

The most succinct result of this study, in that it can be represented by a number, is the methoxy electron affinity. The photodisappearance threshold (1.59 ± 0.04 eV) obtained by Reed and Brauman⁴ remains in good agreement with the number obtained here.

Another derivation of the methoxy electron affinity has been the proton affinity measurement of McIver and Miller,²⁰ later corrected by Bartmess and McIver.²¹ In these ICR experiments, equilibrium constants are measured for the proton transfer between two anions, one with a known proton affinity and the other with an unknown proton affinity to be measured. This involves knowing the internal temperatures of the species, since an equilibrium constant is to be inverted ($\Delta G = -RT \ln K$) into a free energy. The proton affinities obtained by this method are generally consistent and can be handled with a reasonable degree of confidence; for methoxide a proton affinity $\Delta H = -378.4 \pm 1$ kcal/mole is found.²¹ On the other hand, the bond dissociation energy for the neutral reaction



is much less reliable. Bartmess and McIver²¹ have derived an electron affinity for CH₃O from a thermodynamic cycle combining the bond energies for dissociation into ionic and neutral products,

	ΔH	
CH ₃ OH = CH ₃ O ⁻ + H ⁺	+ 378.4 ± 1	kcal/mole (Ref. 20)
H ⁺ + e ⁻ = H	- 313.75	kcal/mole
CH ₃ O + H = CH ₃ OH	- 103.6 ± 2	kcal/mole (Ref. 8)
e ⁻ + CH ₃ O = CH ₃ O ⁻	39.0 ± 2.5	kcal/mole (Ref. 21)

This value differs from our direct determination (36.2 kcal/mole) probably because of the uncertainty in the neutral bond dissociation energy, and we prefer to rewrite the cycle this way

	ΔH	
CH ₃ OH = CH ₃ O ⁻ + H ⁺	+ 378.4 ± 1.0	kcal/mole (Ref. 20)
H ⁺ + e ⁻ = H	- 313.75	

TABLE IV. E.A. corrections (eV).

	CH ₃ O	CD ₃ O	CH ₃ S
Raw E. A.	1.569(6)	1.552(6)	1.894(7)
Rotational correction	0.001(6)	0.000(6)	0.000(6)
Vibrational correction	0.005(20)	0.005(20)	0.000(20)
Spin-orbit	-0.005(4)	-0.005(4)	-0.012(10)
Corrected E. A.	1.570(22)	1.552(22)	1.882(24)

	ΔH
CH ₃ O ⁻ = CH ₃ O + e ⁻	36.20 ± 0.25 kcal/mole (present work)
CH ₃ OH = CH ₃ O + H	100.9 ± 1.0 kcal/mole

Thus we have inverted Bartmess and McIver's procedure²¹ (as originally proposed²²) to obtain a better value for the homolytic bond dissociation energy of CH₃O-H. This corresponds to a heat of formation for CH₃O⁻ of 0.7 ± 1.0 kcal/mole, which disagrees with another recent determination of $\Delta H_f = 3.8 \pm 0.2$ kcal/mole.⁹ However, this latter value was derived from an Arrhenius fit to the kinetics of dimethyl peroxide decomposition. The difference could be explained by assuming an extra 6 kcal/mole activation barrier above the asymptotic product energies (2 CH₃O), contrary to what was assumed in the kinetics experiment.⁹

In a similar manner for the thio compound, we can combine our electron affinity with Bartmess and McIver's proton affinity data to obtain a value of 86.6 ± 1.1 kcal/mole for the S-H homolytic bond dissociation energy in thiomethanol. This resulting bond energy agrees with previous reports.²³

B. CH₃O and CD₃O vibrations:

The vibrational information in the spectrum is mainly that of the C-H umbrella motion. The methoxide spectra are remarkably free of other vibrations. The strong dependence upon deuteration identifies these modes as hydrogenic, while their low frequency (1325 ± 30 cm⁻¹ in CH₃O and 1010 ± 30 cm⁻¹ in CD₃O) marks them as bending motions. The only symmetric mode corresponding to this description is the symmetric umbrella bend, and this forms the basis of our assignment.

The intensity patterns of the mode progressions appearing in the methoxide and deuteromethoxide spectra also are consistent with the vibrational frequency change upon deuteration. The Franck-Condon intensities derived from the methoxide spectrum, combined with the frequency shifts upon deuteration, give the correct intensity pattern for the deuteromethoxide spectrum in a simple one-dimensional harmonic approximation. This is further evidence that only one mode is excited in photodetachment.

The difference in the electron affinities of the hydrogen vs deuterium containing compounds (18 ± 6 meV) is statistically significant. This difference reflects the difference in the force constants for the ion and the neutral. The hydrogens are more constrained in the neutral than in the ion, resulting in about 1000 cm⁻¹ more zero point energy in the neutral methoxy radical than in the ion. This effect perhaps has been observed in the photodetachment of OH,²⁴ but here we have clear evidence of a shift in E.A. upon isotopic substitution. A similar difference (22 meV) was noticed in the proton affinities of CH₃O⁻ and CD₃O⁻, favoring CD₃OH in proton exchange equilibrium.²⁵

By comparing the data of the photodetachment experiment with those of the methoxy optical spectroscopy on

the $\tilde{A}^2A_1-\tilde{X}^2E$ band,^{26,27} a more complete picture of the methoxy radical is obtained. The calculations¹ predict a large C-O bond length change between these two states, lengthening by 0.2 Å in the upper \tilde{A} state. This is consistent with the spectroscopy, in which strong off-diagonal transitions among the vibrational levels of both electronic states are observed. Analysis of the spectrum indicates that this predominantly C-O stretch vibration has a frequency of 500-700 cm⁻¹ in the upper state, and 1000-1100 cm⁻¹ in the lower state. This now provides us with a second vibrational frequency in the \tilde{X}^2E ground state of methoxy, permitting us to say that the C-H symmetric bend ν_2 (obtained from the photoelectron spectrum) is 1325 ± 60 cm⁻¹, while the C-O stretch ν_3 (obtained from the optical spectroscopy) is 1060 ± 90 cm⁻¹.

The frequencies of CH₃O, CH₃O⁻, and the isoelectronic CH₃F are compared in Table V.

C. CH₃S vibrations

The thiomethoxy vibrations (Table III) shows a less regular progression, with at least two modes appearing in the spectrum. The simplest interpretation of the spectrum assigns the 680 and 1450 cm⁻¹ peaks to $v=1$ and $v=2$ of the same mode, with the 1040 cm⁻¹ appearing as $v=1$ of another symmetric mode. Because we lack the deuterated spectrum, it is not possible to identify clearly which of these modes is predominantly hydrogenic, although the most probable identification would be to assign 680 cm⁻¹ to the C-S stretch and 1040 cm⁻¹ to the C-H umbrella bend. Calculations²⁸ indicate the bond length increases by 30% from C-O in methoxy to C-S in thiomethoxy, and this result suggests a significant decrease in the bond strength between the heavy atoms and a decrease in the vibrational frequency.

The optical spectrum of thiomethoxy has been reported²⁹ on the same band system as for methoxy, $\tilde{A}^2A_1-\tilde{X}^2E$. From the optical spectra vibrational frequencies in both the upper (400 cm⁻¹) and lower (675 ± 70 cm⁻¹) state have been reported. This latter frequency agrees quite well with the lowest frequency we observe in the photoelectron spectrum, and the authors²⁹ also assign this to C-S stretch. We would like to caution the use of 400 cm⁻¹ for the upper state vibration: This could also be the difference between the 675 and the 1040 ± 80 cm⁻¹ vibrations which are observed in the photoelectron spectrum. The authors²⁹ do not report assignments of upper state vibrations for other than $v'=0$ and $v'=1$, and both of these persist in fluorescence even at high pressure, leading one to suspect that the features assigned to $v'=1$ may be instead features of the lower state. Another explanation for this doubling of all features in the emission spectrum could be a large spin-orbit splitting in this 2E state, an explanation also likely to explain an observed doubling of the photodetachment threshold.¹⁹ This question could be addressed by further optical experiments, and would be particularly amenable to laser induced fluorescence spectrometry.³⁰

Our knowledge of the CH₃S vibrations is summarized

in Table V. We would like to emphasize that this assignment is not secure, especially with respect to the assignment of 1040 cm⁻¹ to the vibration ν_2 . Higher resolution work in progress¹⁹ and deuteration may be helpful in making firm assignments.

D. Spin and Jahn-Teller effects

ESR studies of methoxy radical have proven to be difficult primarily because of its extreme reactivity.^{31,32} Thus, although methoxy is produced in pulse radiolysis of methanol, it rapidly abstracts a hydrogen from the parent compound, forming the hydroxymethyl radical $\dot{\text{C}}\text{H}_2\text{OH}$ instead. Because of this reactivity only a matrix-isolation study is expected to yield ESR data on this interesting reactive intermediate. Yet even under these conditions the task is difficult: It has been suggested³³ that the spin-orbit coupling would increase the relaxation rate and broaden the lines to the point of unobservability. Only recently, at 4.7 K in a crystal host has the methoxy ESR been observed.³⁴ The electron g factor is almost the same as that in OH under similar conditions, not as large as would be expected for a free spin in a Π state.³⁵ This has been explained by assuming a large interaction of the radical with the site, causing a splitting of the Π degeneracy and quenching the spin-orbit interaction. Thus it is difficult to derive the free-molecule parameters from the solid state ESR data.

Microwave spectroscopy of this radical may also be elusive for similar reasons of its reactivity and low available densities in the gas phase. So far, the only experiments giving possible structural information are the laser magnetic resonance measurements¹⁷ on this species, but these await analysis.

The magnitude of the Jahn-Teller effect³⁶ in methoxy has been calculated¹ in a limited geometry search. When the C-O axis was tilted relative to the plane of the three hydrogens, a minimum was found for a 2.5° displacement from the perpendicular, corresponding to a slightly "staggered" configuration in which the oxygen tries to nestle between two of the hydrogens. This effect is small. The first- and second-order Jahn-Teller linear coupling coefficients^{37,38} obtained by fitting the calculations¹ to a second order expression³⁸ shows that the first-order coupling is almost negligible ($k_1^2 = 0.04$), while the second-order coupling coefficient seems to dominate ($k_2^2 = 0.12$), making the effect almost entirely a second-order Renner-Teller effect. So far no experiments have seen any evidence of a geometry distortion caused by the Jahn-Teller effect in this molecule. Our photoelectron spectra gives no indication of any "Jahn-Teller modes," the nonsymmetric e vibrations, which would be induced by break-down of the molecular symmetry. Although these Jahn-Teller modes have been observed in photodetachment of another system³⁹ in which the linear coupling was small ($k^2 \leq 0.5$), in this case the linear coupling appears to be much smaller ($k_1^2 \leq 0.1$ approximately) in agreement with the calculations.

A small Jahn-Teller effect is also consistent with

TABLE V. Vibration frequencies (cm⁻¹).

Species	ν_1 C-H str. (a_1)	ν_2 H umbrella (a_1)	ν_3 C-O str. (a_1)	ν_4 C-H str. (e)	ν_5 H bend (e)	ν_6 rock (e)
CH ₃ O		1325(30) ^a	1060(90) ^b			
CH ₃ O ⁻		1075(100) ^a				
CH ₃ F	2930	1464	1049	3006	1467	1182 ^d
CD ₃ O		1020(30) ^a				
CD ₃ O ⁻		915(100) ^a				
CD ₃ F	2110	1136	991	2258	1072	903 ^d
CH ₃ S ⁻		1040(80) ^a	680(40) ^a 670(75) ^c 625(80) ^a			
CH ₃ S ⁻	2937	1355	732	3042	1452	1017 ^d

^aThis work.

^bReference 27.

^cReference 29.

^dReference 40.

intuition about the methoxy radical. The doubly degenerate orbital that causes the electronic degeneracy is predominately an oxygen p -type orbital, while the Jahn-Teller modes which would split this degeneracy are hydrogen motions. Yet the Jahn-Teller effect cannot be dismissed entirely in this radical, since it should profoundly influence all high resolution measurements of the rotational levels, the spin-orbit coupling, and even the nuclear hyperfine splittings.

V. CONCLUSION

Methoxy radical has been investigated by photoelectron spectrometry of its negative ion. Information derived from this investigation include its electron affinity (1.570 ± 0.022 eV) and frequencies of vibration produced in the detachment process. By also investigating the deuterated species (E.A. = 1.552 ± 0.022 eV) these vibrations are determined to be mainly hydrogenic. Thus we conclude that the predominant change in the geometry upon detachment of the negative ion is a hydrogen displacement, probably toward the oxygen as indicated by calculations.¹ A Jahn-Teller effect in the neutral \bar{X}^2E state is too small to affect the spectra that were observed.

The striking difference in the C-O and C-S bonds shows clearly in the spectra of the methoxy and thio-methoxy spectra. The thiomethoxy radical has a significantly different set of vibrations excited in the detachment of its negative ion, with fewer hydrogen vibrations and more C-S motion. Overall, the vibrational progression development is less, indicating that the neutral and ion geometries are more alike in CH₃S than in the case of methoxy and its ion. Furthermore, a larger CH₃S electron affinity is obtained, 1.882 ± 0.024 eV. Our knowledge of the vibrations in the species studied is summarized in Table V.

Finally, the electron affinities of the species observed in these experiments are combined with proton affinities measured elsewhere^{20,21} to obtain more accurate values of the neutral bond dissociation energies for the parent alcohols of these species. Thus for methyl alcohol dissociating into hydrogen and methoxy in the gas phase, a bond strength of 100.9 ± 1 kcal/mole results, while

for the thio substituted alcohol CH₃SH the bond strength of only 86.6 ± 1.1 kcal/mole results.

This study illustrates some applications of photodetachment electron spectrometry to the study of radical species.

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