acetone molecular ions retain large amounts of internal energy for more than 30 μ s after formation by electron impact. (2) These highly excited ions are the dominant CID reactants at such low collision energies. (3) These low-energy (0.45- and 0.65-eV) collisions trigger the release $(E \rightarrow T)$ of about 2.9 eV of stored energy into the recoil of the acetone ion and the collider He atom. With reference to the initial ion beam direction, the acetone ions are backward scattered and He atoms are forward scattered in the CM coordinate frame. (4) The recoiling acetone molecular ion rapidly dissociates into acetyl ion and methyl radical with low kinetic energy of separation. We infer from these observations that the collision process triggers the $A \rightarrow X$ conversion of the acetone molecular ion with the release of most (perhaps all) of the stored electronic energy as translational energy. The vibrationally excited ion then dissociates from the ground-state hypersurface. Our continuing research on polyatomic ion CID dynamics will address the question whether electronically excited states are also important intermediates at higher collision energies.

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Spectroscopic Observation of the $CH_2(\tilde{a}^1A_1)$ Radical in the Reaction of C_2H_2 with O Atoms

J. Peeters,* S. Vanhaelemeersch, J. Van Hoeymissen, R. Borms, and D. Vermeylen

Department of Chemistry, K.U. Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium (Received: February 13, 1989)

Direct spectroscopic observation of the CH₂($\tilde{a}^{1}A_{1}$) radical in C₂H₂/O/H systems (T = 295 K) is reported for the first time. Characteristic rotational features of the ${}^{1}B_{1}(0,14,0) \leftarrow {}^{1}A_{1}(0,0,0)$ excitation spectrum were positively identified by laser-induced fluorescence. The absolute $CH_2({}^{1}A_1)$ concentration was estimated by a calibration based on the $CH_2CO \rightarrow CH_2({}^{1}A_1)$ + CO photodissociation at 308 nm. The experimental evidence supports formation of singlet CH₂ in C₂H₂/O/H systems by the fast reaction of H atoms with the HCCO radical, known to be the major product of the primary C_2H_2 reaction.

Introduction

The three most recent measurements¹⁻³ of the branching fraction of the elementary reaction of C_2H_2 with O atoms:

$$C_2H_2 + O \rightarrow HCCO + H$$
 (1a)

$$\rightarrow CH_2(X^3B_1) + CO$$
 (1b)

all yield k_{1a}/k_1 values in the range 0.60–0.83, at temperatures from 300 to 2500 K. Theoretical predictions also favor reaction 1a as the dominant channel, independent of temperature.⁴ Thus, it is imperative to incorporate subsequent reactions of the HCCO radical with O atoms and H atoms in ethyne oxidation schemes as pointed out by Peeters et al.;1 they specifically emphasized the likelihood that the very fast HCCO + H reaction⁵ leads to CH_2 in its metastable singlet $\tilde{a}^1 A_1$ state:

$$HCCO + H \rightarrow H_2CCO^{\dagger} \rightarrow CH_2(\tilde{a}^1A_1) + CO$$
 (2)

The $CH_2({}^{1}A_1)$ radical as opposed to the ground-state X^3B_1 is highly reactive to closed shell molecule;6-10 in hydrocarbon flames, where C_2H_2 is an important intermediate, the singlet methylene

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radical will contribute to the formation of higher unsaturated hydrocarbons by fast reactions with $C_2H_2^{8,9}$ and with polyacetylenes.

We have already reported^{3,11} experimental evidence, albeit of an indirect nature, for the formation of singlet CH₂ by reaction 2, both in $C_2H_2/O/H$ and in C_3O_2/H systems (with HCCO + CO as primary reaction products in the latter). The evidence is based on the observed strong reduction of molecular beam mass spectrometric (MBMS) CH₂ signals upon addition of CH₄, which at 300 K is quasi-inert toward $CH_2({}^{3}B_1)$, but highly reactive toward $CH_2(^{\overline{1}}A_1)$.^{6,7}

The prime objective of the present investigation was to obtain conclusive proof for the presence of $CH_2({}^1A_1)$ in $C_2H_2/O/H$ systems by laser-induced fluorescence. The second aim was to evaluate its concentration and to compare it with the value predicted by the proposed formation scheme.

Experimental Section

A schematic drawing of the equipment is shown in Figure 1. Ethyne ($\simeq 0.01$ mbar) was reacted with O/H mixtures (both in the 0.002-0.01 mbar range), in a 2.8 cm diameter quartz flow reactor at T = 295 K, $p_{tot} \simeq 1$ mbar (He as diluent gas), and flow speed $v \simeq 1000$ cm s⁻¹. The atoms were generated by a microwave discharge through $O_2/H_2/He$ mixtures; dissociation yields were measured by the MBMS technique. Ethyne was added through a movable central injector tube.

A baffled probe laser beam (0.6 cm diameter) passes 1 cm downstream of the reactor mouth at right angles. The pulsed probe beam is generated by a tunable dye laser pumped by a Nd:YAG pump laser (Quantel Datachrome 5000 system). The characteristics are $E_p \simeq 10 \text{ mJ/pulse}$ at $\lambda = 585-593 \text{ nm}$, $\tau_p = 13 \text{ ns}$, bandwidth = 0.1 cm⁻¹, and $\nu_{rep} = 10 \text{ Hz}$. The energy density drives

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Figure 1. Schematic illustration of the equipment. The excimer laser beam (not shown) is perpendicular to the dye laser beam and to the fluorescence collection optics axis.

the CH₂ $\tilde{b}^1 B_1 \leftarrow \tilde{a}^1 A_1$ transition well into saturation.

Fluorescence, at right angles with the probe beam, is focused through a RG-610 high-pass filter onto a Hamamatsu R 928 PM tube. The signal is fed to an SRS 280 boxcar integrator; data acquisition/reduction is achieved by a Macintosh II through a Nat. Instr. NB-D10-24 interface supported by Labview software.

Reference $CH_2(^1A_1)$ excitation spectra were obtained by photolysis of ketene at 308 nm using a XeCl excimer laser (Lambda Physik EMG 101 MSC; $E_p \simeq 60 \text{ mJ/pulse}$) crossing the LIF cell at right angles to both the probe laser beam and to the fluorescence collection axis. The delay between the photodissociation pulse and the probe pulse is controlled by a home-built digital delay generator.¹² The time delay (5 μ s) and the mixture composition (0.002-0.005 mbar ketene and 0.66 mbar helium) ensure a $CH_2({}^1A_1)$ rotational energy distribution close to 295 K thermal equilibrium.13

Results and Discussion

The most intense lines observed in the excitation spectrum of $CH_2(^1A_1)$ generated by 308-nm ketene photolysis correspond to the ${}^{1}B_{1}(0, 14, 0)4_{04} \leftarrow {}^{1}A_{1}(0, 0, 0)4_{14}$ transition at 590.71 nm and the $(0,14,0)4_{04} \leftarrow (0,0,0)3_{12}$ transition at 589.37 nm, in agreement with absorption measurements by Petek et al.14

At dye laser wavelengths fixed at either of the above values, weak fluorescence was also observed in $C_2H_2/O/H$ systems, with a signal level about 2 orders of magnitude lower than obtained in the ketene photodissociation experiments.

It was ascertained that the signals were not due to CH₂ generated by probe-laser-induced multiphoton dissociation of ketene formed in the $C_2H_2/O/H$ reaction: no fluorescence was observed when ketene at $p \simeq 0.05$ mbar was irradiated by the probe laser only.

Next, all experimental circumstances and instrumental factors affecting the S/N ratio of the $C_2H_2/O/H$ system signals were optimized carefully, i.e., the mixture composition, the reaction time (determined by the distance between the C_2H_2 -O/H mixing point and the probe laser beam), the fluorescence collection optics, the PM voltage (800 V), the boxcar gate delay (50 ns effective), and the gate width (350 ns).

After the optimization, the two strongest lines of the $CH_2(^1A_1)$ excitation spectrum could be clearly identified when scanning the dye laser wavelength at 10⁻³ nm s⁻¹, the lowest possible scan rate. Multiple scans (10-20) were then made over two short spectral regions comprising characteristic groups of $CH_2({}^{1}A_1)$ excitation lines including the two most prominent peaks mentioned above; the regions chosen were 589.075-589.525 and 590.625-590.775 nm. The multiple scans were summed, after slight wavelength shifts $(1-10 \times 10^{-3} \text{ nm})$ on the basis of the $4_{04} \leftarrow 3_{12}$ or $4_{04} \leftarrow$ 4_{14} line maxima locations as observed for the individual scans; such shifts were necessitated by dye laser wavelength drift.



HAVELENGTH (NM)

Figure 2. Upper trace: LIF excitation spectra for a $C_2H_2/O/H/He$ mixture 0.008/0.011/0.003/1.25 mbar; reaction time $\simeq 2$ ms. Lower trace: parts of the ${}^{1}B_{1} \leftarrow {}^{1}A_{1}$ excitation spectrum of $CH_{2}({}^{1}A_{1})$ generated by 308-nm photodissociation of ketene; $(0,14,0) \leftarrow (0,0,0)$ band; tran-Solution in proceeding (c), (3, 1, 2) (c), (3, 2) (c), (3, 3) (c)

The signal/noise enhancement achieved by the summation procedure brought to light detailed spectral features. As an example Figure 2 shows the sum of 12 scans for a $C_2H_2/O/H/He$ mixture with initial partial pressures 0.008/0.011/0.003/1.25 mbar at an (optimum) reaction time of 2 ms. The origin of the salient rotational structure must undoubtedly be ascribed to $CH_2({}^{1}A_1)$, as demonstrated by comparison with the singlet methylene reference spectra shown at the bottom of the figure (rotational transitions are assigned in accordance with Petek et al.¹⁴).

An estimate of the singlet CH_2 concentration in $C_2H_2/O/H$ systems was made by calibration of the signal strengths against the values obtained for $CH_2(^1A_1)$ formed by laser photolysis of ketene. The signal strength for a 0.004 mbar of ketene/0.66 mbar of He mixture was a factor 70 larger than for the $C_2H_2/O/H$ system of Figure 2. With a known photodissociation cross section of 3×10^{-20} cm² at 308 nm¹⁵ (yielding solely singlet CH₂¹⁶), a measured excimer laser pulse energy of 60 mJ, and a beam section of 2 cm², the fraction of ketene dissociated to $CH_2({}^{1}A_1)$ is 1.4 \times 10⁻³, with 60% observed to remain after 5 μ s (decay time constant = $10 \ \mu s$).

Of course, one should take into account the ratio of the relative populations of the (0,0,0) vibration state for singlet CH₂ generated by 308-nm ketene photolysis on the one hand and singlet CH₂ formed in $C_2H_2/O/H$ systems by reaction 2 on the other hand. According to Nesbitt et al.,¹⁷ the powerful "separate statistical ensemble" (SSE) model of Wittig et al.,¹⁸ applicable to dissociation processes without exit barrier, predicts a (0,0,0) population of 70% for the 308-nm photolysis of ketene; our SSE calculation yields a (0,0,0) population of only 22% for singlet CH₂ produced by reaction 2, the difference being due to the higher exoergicity of the latter process (see below). The lifetime of $CH_2({}^{1}A_1)$ in the $C_2H_2/O/H$ system of Figure 2 is about 5 μ s (governed mainly by singlet \rightarrow triplet intersystem crossing collision with He bath gas atoms^{6,7}) implying about 50 collisions, sufficient to ensure rotational relaxation, but far too low for vibrational relaxation of (1,0,0), (0,1,0), or (0.0.1) states to the ground state. Disregarding the combined differences in the effective fluorescence volumes and ${}^{1}B_{1}$ fluorescence yields between the two systems (estimated to be $\leq 40\%$), one finally obtains an approximate total $CH_2({}^{1}A_1)$ concentration in the $C_2H_2/H/O$ system of Figure 2 of 3.8×10^9 molecules cm⁻³.

On the other hand, the singlet methylene concentration in the Figure 2 mixture was computed assuming $CH_2({}^{1}A_1)$ formation

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by reaction 2 with a rate constant value⁵ of $k_2 = 1.3 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The rate constants for the pertaining C₂H₂-HC-CO- and CH₂(¹A₁) reactions were taken from the current literature;¹⁻⁹ k values for the less important singlet CH₂ removal processes by O and H atoms were estimated to be 1.3×10^{-10} and 2.5×10^{-10} cm³ molecule⁻¹ s⁻¹, respectively. The model predicts [CH₂(¹A₁)] $\simeq 4.3 \times 10^9$ molecules cm⁻³ at its t = 2 ms maximum, i.e., nearly equal to the (approximate) measurement.

An important additional observation is that at short reaction times (≤ 2 ms) the CH₂(¹A₁) signals vanish upon removing hydrogen from the reaction mixture; this lends support to the proposed singlet CH₂ formation reaction 2 and rules out direct formation by the primary C₂H₂ + O reaction.

As anticipated above, the likely mechanism of reaction 2 is an HCCO + H combination process leading to vibrationally excited ketene in the singlet ground state which then rapidly fragments into $CH_2({}^{1}A_1) + CO$. Thus, the mechanism is quite similar to that for ketene photodissociation at 308 nm,¹⁸ where CH_2 is formed solely in the singlet state.¹⁶ There is, however, a difference in the vibrational energy content of the $CH_2CO^{\dagger}({}^{1}A_1)$ molecule: in the 308-nm photolysis process it is 93 kcal/mol whereas in the

chemical activation reaction 2 it is about 105 kcal/mol, using $\Delta H_{\rm f}({\rm HCCO}) = 42$ kcal/mol¹⁹ and $\Delta H_{\rm f}({\rm CH_2CO}) = -11$ kcal/mol.²⁰ Thus in the latter case the lifetime for fragmentation will be even shorter and hence singlet \rightarrow triplet intersystem crossing even less probable. Also, the excess energy available to the fragments is only 7 kcal/mol in the 308-nm photolysis, ^{16,17} whereas it is 19 kcal/mol for reaction 2; as a consequence, in the latter process a smaller fraction of the singlet CH₂ will arise in the (0,0,0) vibrational ground state.

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Persistent Spectral Hole Burning of Molecular Clusters in a Supersonic Jet

Robert J. Lipert and Steven D. Colson*

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511 (Received: February 15, 1989; In Final Form: April 3, 1989)

A spectroscopic technique is presented that applies the principles of persistent spectral hole burning to the study of weakly bound clusters formed in a supersonic jet expansion. This approach allows one to distinguish unambiguously between homogeneous and heterogeneous structure in the electronic spectra of mass-selected clusters. Moreover, it makes possible the observation of the electronic spectrum of a single isomer which would otherwise be embedded in the spectra of other isomers. The technique is tested using a mixture of cis and trans isomers of *m*-cresol. It is then used to establish that the spectrum of the phenol-ethanol hydrogen-bonded complex, in the region of the S_1 state origin, is due to only a single isomer. The reassignment of the rich vibronic structure near the origin is discussed. Potential applications of this technique in other areas of spectroscopy are briefly considered.

Introduction

The ultraviolet-visible absorption spectra of even the simplest van der Waals and hydrogen-bonded clusters formed from polyatomic molecules are often quite complex.¹ This spectral congestion may be due to the activity of low-frequency vibrations involving the cluster bonds, the presence of clusters of various sizes with electronic states of similar energy, or the existence of a number of isomeric forms of clusters of the same composition. Multiphoton ionization mass spectrometry can sometimes unfold the overlapping spectra of species with different masses when it is possible to avoid fragmentation of the clusters. The result is then a simplification of the spectra and an unambiguous assignment of the stoichiometry of the clusters responsible for the spectra.² However, these spectra may still contain many peaks and there remains the uncertainty of whether this structure is homogeneous, i.e., due to low-frequency intermolecular vibrational modes of a single cluster, or heterogeneous, i.e., due to overlapping spectra of various cluster isomers. One means of resolving this question is through rotational analyses. However, only a few structures of clusters containing large molecules have been obtained from rotationally resolved spectra.³ This is in part because

sub-Doppler methods are required for the generation of these spectra.

In response to this problem, we have developed a spectroscopic technique that can resolve the spectrum of a single cluster isomer in the presence of other isomers that absorb in the same region. Likewise, it can unambiguously rule out cluster isomers as a source of spectral congestion. The ability to go beyond the mass-selective spectroscopy of clusters to isomer-selective spectroscopy holds great promise for contributing to the understanding of dynamical processes in clusters such as cluster isomerization.⁴ The technique is based on the principles of laser hole burning,⁵ in this case applied in the cold, collision-free environment of a supersonic expansion. Our approach exploits the fact that, subsequent to electronic excitation by laser irradiation, relatively few molecules find their way back to the initial rovibronic levels spanned by the bandwidth of the excitation laser. Photophysical processes such as internal conversion, intersystem crossing, emission to other levels, and ionization by absorption of an additional photon as well as photochemical processes such as predissociation and isomerization

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