Detection of methylene (X 3B1) radicals by 3 + 1 resonance-enhanced multiphoton ionization spectroscopy

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a 0.01-eV width Lorentzian function, accounting for the experimental resolution. The spectrum presents a main regular progression (ω = 540 cm^{-1}) broadened by thermal effects. As shown in Figure 3, the bound–free transitions correspond to broad bands. Such excitations lead to dissociation of a H_2O^+ fragment.

In conclusion, the experimentally reported[3,4] $Zn^+(H_2O)$ cluster can be used as precursor of the $Zn^{2+}(H_2O)$ cluster under ultraviolet photoionization around 79.8 nm. Such an experiment could be extremely selective (in producing $Zn^{2+}(H_2O)$), using synchrotron

radiation. Otherwise, concentrations of different products may be analyzed when using UPS. This strategy could also be applied in order to obtain other doubly charged transition metal cations hydrated with a small number of water molecules.

Detection of CH₂(X̃ ³B₁) Radicals by 3 + 1 Resonance-Enhanced Multiphoton Ionization Spectroscopy

Karl K. Irikura[†] and Jeffrey W. Hudgens*

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology,[‡] Gaithersburg, Maryland 20899 (Received: December 2, 1991)

Spectra of triplet methylene radicals, X̃ ³B₁ CH₂ and CD₂, were produced between 380 and 440 nm using mass-resolved resonance-enhanced multiphoton ionization (REMPI). These spectra arose from three-photon resonances with the B̃ ³A₂ (3d), C̃ (3d), D̃ (3d), and 4d ³A₂ Rydberg states between 78 950 and 68 200 cm^{-1} above the ground state. A fourth laser photon ionized the radicals; i.e., CH₂$^+$ (*m/z* 14) and CD₂$^+$ (*m/z* 16) ion signals were generated through a 3 + 1 REMPI mechanism. Methylene radicals were produced by the reaction of fluorine atoms and methyl radicals.
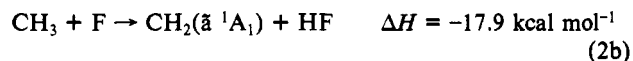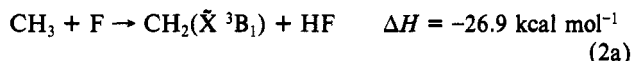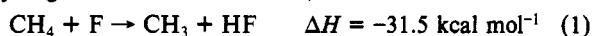
Methylene radicals, CH_2 and CD_2, play important roles in the combustion and photochemistry of numerous chemical systems. Because the first excited state of CH_2, the ã ¹A₁ state, lies at low energy (T_0 = 3147 cm^{-1}),[1] an understanding of CH_2 chemistry requires studies of both the X̃ ³B₁ and ã ¹A₁ states. Ground-state methylene radicals are particularly inconvenient to study. Although kineticists have used laser magnetic resonance spectroscopy with great success to measure reaction rates of CH₂(X̃ ³B₁),[2] this technique is not adaptable to most other experiments, e.g., molecular beam studies of reaction dynamics. Laser-induced fluorescence (LIF) spectroscopy can detect CH₂(ã ¹A₁),[3] but no similar LIF detection scheme for CH₂(X̃ ³B₁) is available. Furthermore, all known optical absorptions of CH₂(X̃ ³B₁) reside in the vacuum-ultraviolet (vacuum-UV) spectral region.[4,5] The experimental difficulties incumbent to vacuum-UV optics prevent experimentalists from using transient absorption spectroscopy to measure concentrations of CH₂(X̃ ³B₁).

In this work we report a new laser-based method for detecting CH₂(X̃ ³B₁) and CD₂(X̃ ³B₁) based upon resonance-enhanced multiphoton ionization (REMPI) spectroscopy. In our detection scheme we enhance the multiphoton ionization cross section of CH₂(X̃ ³B₁) with an intense, tightly focused laser beam. CH_2 is excited into the B̃, C̃, and D̃ electronic states through simultaneous absorption of three identical laser photons. The excited CH_2 may ionize and form CH₂$^+$(X̃ ²A₁) by subsequently absorbing one more laser photon; i.e., we use a one-color 3 + 1 REMPI excitation scheme. The present REMPI detection scheme uses lasers and optics common to many modern laboratories. We believe that REMPI detection will be useful for the sensitive and selective detection of gas-phase CH₂(X̃ ³B₁) radicals in many other experiments.

The apparatus and procedures used to record the REMPI spectra have been described in detail previously.[6] In brief, in a flow reactor free radicals are produced by the reaction of fluorine atoms with various reagents. Upstream from this flow reactor fluorine atoms are produced with a microwave discharge of 3–5% F_2 in helium. The total pressure in the flow reactor is ~100–300

Pa (~2–3 Torr). The radicals effuse from the flow reactor into the ionization region of a time-of-flight mass analyzer (1–10 mPa). Radicals are ionized by the focused output of an excimer-pumped tunable dye laser (energy = 8–16 mJ/pulse; bandwidth = 0.2 cm^{-1}, fwhm; focal length = 75 mm). The ions are mass resolved, gated integrators monitor selected ion masses, and a computer data-acquisition system records and averages the selected ion intensities as a function of laser wavelength. The spectra shown here are composites of spectra obtained with the laser dyes (Exciton Chemical Co.)[7] PBBO (385–405 nm), DPS (399–415 nm), and Stilbene 420 (415–440 nm). The spectra are uncorrected for the variation in laser pulse energy which occurs over the range of each dye.

Methylene radicals are presumably generated by a sequence of hydrogen abstraction reactions, reactions 1 and 2.[8] The

$$CH_4 + F \rightarrow CH_3 + HF \qquad \Delta H = -31.5 \text{ kcal mol}^{-1} \quad (1)$$

$$CH_3 + F \rightarrow CH_2(\tilde{X}\,^3B_1) + HF \qquad \Delta H = -26.9 \text{ kcal mol}^{-1} \tag{2a}$$

$$CH_3 + F \rightarrow CH_2(\tilde{a}\,^1A_1) + HF \qquad \Delta H = -17.9 \text{ kcal mol}^{-1} \tag{2b}$$

(1) Jensen, P.; Bunker, P. R. *J. Chem. Phys.* **1988,** *89,* 1327.

(2) Seidler, V.; Temps, F.; Wagner, H. Gg.; Wolf, M. *J. Phys. Chem.* **1989,** *93,* 1070.

(3) (a) Danon, J.; Filseth, S. V.; Feldmann, D.; Zacharias, H.; Dugan, C. H.; Welge, K. H. *Chem. Phys.* **1978,** *29,* 345. (b) Lengel, R. K.; Zare, R. N. *J. Am. Chem. Soc.* **1978,** *100,* 7495. (c) Ashfold, M. N. R.; Fullstone, M. A.; Hancock, G.; Ketley, G. W. *Chem. Phys.* **1981,** *55,* 245. (d) Petek, H.; Nesbitt, D. J.; Ogilby, P. R.; Moore, C. B. *J. Phys. Chem.* **1983,** *87,* 5367. (e) Sappey, A. D.; Crosley, D. R.; Copeland, R. A. *Appl. Phys. B* **1990,** *50,* 463.

(4) (a) Herzberg, G. *Proc. R. Soc. (London)* **1961,** *A262,* 291. (b) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc. (London)* **1966,** *A295,* 107. (c) Herzberg, G.; Johns, J. W. C. *J. Chem. Phys.* **1971,** *54,* 2276. (d) Herzberg, G. *J. Mol. Struct.* **1990,** *217,* xi.

(5) Herzberg, G. *Can. J. Phys.* **1961,** *39,* 1511.

(6) Johnson, R. D. III; Tsai, B. P.; Hudgens, J. W. *J. Chem. Phys.* **1988,** *89,* 4558.

(7) Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

* Address correspondence to this author.
[†] NIST/NRC Postdoctoral Associate.
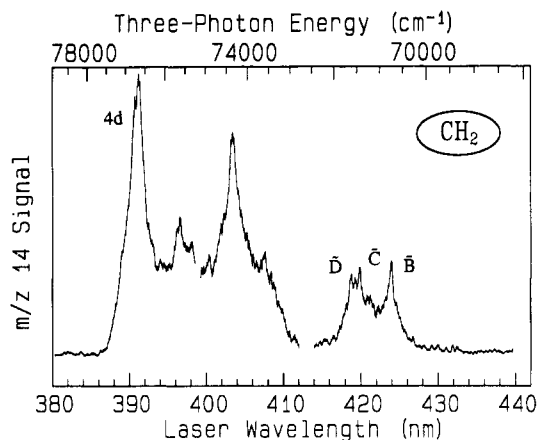[‡] Formerly called the National Bureau of Standards.

Figure 1. Composite m/z 14 REMPI spectrum of the $CH_2(\tilde{X}\ ^3B_1)$ observed between 380 and 440 nm.

Figure 2. Composite m/z 16 REMPI spectrum of the $CD_2(\tilde{X}\ ^3B_1)$ observed between 380 and 440 nm.

branching ratio of reaction 2 is not known. However, we conjecture that the flow reactor effluent contained greater amounts of $CH_2(\tilde{X}\ ^3B_1)$ than of $CH_2(\tilde{a}\ ^1A_1)$, since $CH_2(\tilde{a}\ ^1A_1)$ is both thermodynamically and kinetically less stable than $CH_2(\tilde{X}\ ^3B_1)$.[9] Inelastic collisions will quench $CH_2(\tilde{a}\ ^1A_1)$ to form $CH_2(\tilde{X}\ ^3B_1)$.[9]

Figure 1 shows the spectrum carried by CH_2^+ (m/z 14) between 380 and 400 nm. All evidence indicates that this spectrum originates from REMPI of CH_2. The CH_2^+ signal disappears in the absence of methane, or if the microwave discharge that generates fluorine atoms is extinguished. When the methane is replaced with isotopically labeled CD_4, the REMPI spectrum is carried by CD_2^+ (m/z 16), as shown in Figure 2.

As expected from the $F + CH_4$ reaction system, the REMPI mass spectra of the reactor effluent showed evidence of numerous chemical reactions. REMPI spectra of CF, CH, CH_3, and CH_2F radicals were identified.[10-12]

Figures 1 and 2 bear comparison with the known triplet states of CH_2. The $\tilde{B}\ ^3A_1$ (3d), $\tilde{C}$ (3d), and $\tilde{D}$ (3d) states are diffuse bands located at $T_0 = 70\,634$, $70\,917$, and $71\,592$ cm^{-1}, respectively.[4,5] In three-photon absorption spectra, transitions to these excited states from the $\tilde{X}\ ^3B_1$ state should appear at 424.6, 422.9, and 418.9 nm, in fair agreement with Figure 1. The $\tilde{B}\ ^3A_2$ state is the first member of a 3d Rydberg series. The second series
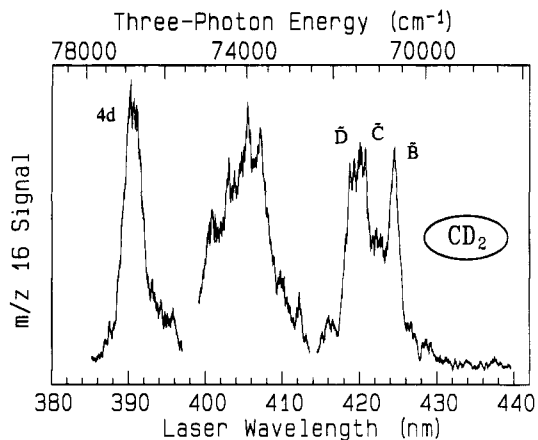
member, the 4d $^3A_2$ state, lies near 76 553 cm^{-1}.[4,5] In a three-photon absorption spectrum this state should appear at 391.8 nm, again in fair agreement with Figure 1. Our confirmation of these four previously known bands is strong evidence that the spectrum is that of CH_2. We note that exact agreement with the literature T_0 values is not expected. These band locations are based upon intensity maxima rather than rotational analyses. Furthermore, the increased number of rotational branches characteristic of three-photon spectra will produce a band contour that differs from the one-photon vacuum-UV spectrum.

The spectrum carried by CH_3^+ (or CD_3^+)[12] was monitored simultaneously with that carried by CH_2^+ (or CD_2^+). Comparison of the m/z 15 (or m/z 18) spectrum with the m/z 14 (or m/z 16) spectrum indicates clearly that the four bands discussed above do not originate from CH_3^+. CH^+ (m/z 13), on the other hand, does appear to carry some of the peaks of the CH_2 REMPI spectrum. CH^+ may arise through photolysis of CH_2^+ in this spectral region.

The features located near 396.5 and 403.5 nm (Figure 1) have not been reported previously. We cannot assign their photon order at this time. We are cautious to assign the 403.5-nm peak to REMPI of CH_2 since the CH_3^+ spectrum also has a broad feature at that wavelength. We intend to pursue this by using alternative methods of radical production, such as ketene photolysis, to generate the CH_2 radicals.

We have reported the first optical detection method for the $CH_2(\tilde{X}\ ^3B_1)$ radical that uses lasers common to many laboratories. Currently, we are extending our studies to expand the spectral region examined. We expect that CH_2 will produce extensive 2 + 1 and 3 + 1 REMPI spectra, leading to an increased understanding of the electronic structure of CH_2.

(8) Thermochemical values are derived from: (a) Lias, S. G.; Bartmess, J. E.; Holmes, J. L.; Levin, R. D.; Liebman, J. F.; Mallard, G. *J. Phys. Chem. Ref. Data* **1988**, (Suppl. Ser. No. 1). (b) Reference 1.

(9) Laufer, A. H. *Rev. Chem. Intermed.* **1981**, *4*, 225.

(10) Johnson III, R. D.; Hudgens, J. W. *J. Phys. Chem.* **1987**, *91*, 6189.

(11) Hudgens, J. W.; Dulcey, C. S.; Long, G. R.; Bogan, D. J. *J. Chem. Phys.* **1987**, *87*, 4546.

(12) DiGiuseppe, T. G.; Hudgens, J. W.; Lin, M. C. *J. Phys. Chem.* **1982**, *86*, 36.