

Electronic emission due to collisions involving low energy CHO^+ and H^+ ions and CH_4 and N_2 molecules

A Michael, P Misra, A Farah and V Kushawaha

Laser Physics Laboratory, Department of Physics and Astronomy, Howard University, Washington, DC 20059, USA

Received 23 December 1991

Abstract. Electronic emission from CH and OH radicals, CH^+ , CO^+ and N_2^+ ions and atomic hydrogen lines have been observed during collisions of CHO^+ and H^+ ions with CH_4 and N_2 molecules in the laboratory kinetic energy range 100-900 eV. Emission cross sections of the excited CH radicals, N_2^+ ions and H_β transition of H atoms have been measured in the above energy range.

1. Introduction

Ion-molecule reactions involving collisions of ground and/or excited state species have been a subject of increasing interest in the past (Bowers 1986, Fontijn 1985, Franklin 1972), mainly because of their direct involvement in the complex chemistry/physics of fuel-rich hydrocarbon flames, interstellar chemistry, discharge and laser-initiated plasmas, etc. The chemi-ionization processes have been predicted to be the leading cause of soot formation in oxy-hydrocarbon flames. Ions such as CHO^+ and C_3H_3^+ have been postulated to be the root cause of soot formation in fuel-rich flames. According to Calcote (1981), the CHO^+ ions are formed due to associative ionization of $\text{CH}(\text{X}) + \text{O} \rightarrow \text{CHO}^+ + \text{e}$ with a rate constant of $k = 2.3 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in the temperature range 2000-2400 K (Peeters and Vinckier 1975). Here $\text{CH}(\text{X})$ is the ground-state of the CH radical. However, Phippen and Bayes (1989) and Bayes (1988) have recently shown that involvement of the metastable $\text{CH}(\text{a } ^4\Sigma^-)$ rather than the ground state $\text{CH}(\text{X})$ radical is a strong possibility in the formation of CHO^+ ions. The $\text{CH}(\text{a } ^4\Sigma^-)$ states lies $\approx 0.69 \text{ eV}$ above the ground state $\text{CH}(\text{X } ^2\Pi)$ (Neils *et al* 1988). Cool and Tjossem (1984) have shown enhancement of the above rate constant by a factor of over 2000 with electronically excited state $\text{CH}(\text{A } ^2\Delta)$ or $\text{CH}(\text{B } ^2\Sigma^-)$ radicals. In a hydrocarbon-air flame, a large number of ground state as well as excited state CH radicals (in addition to many other radicals such as C_2 , OH, etc) are expected to be observed and have, in fact, been observed by many previous investigators (Calcote 1981, Peeters and Vinckier 1975, Miller 1976, Le and Vanpee 1985). Therefore, a large number of CHO^+ ions are expected to be present in the flame front. In addition to CHO^+ ions, other ions such as H_3O^+ and C_3H_3^+ have also been observed in flame fronts and their concentration is many times greater than the concentration of CHO^+ ions (Calcote 1981). The loss of the CHO^+ ions is a direct result of fast ion-molecule reactions in the flame medium. At a flame temperature of 2000-4000 K, several processes such as chemi-excitation, chemi-ionization, ion-molecule reactions, ionization due to collisions of excited state species and thermal

electrons, superelastic collisions involving hot electrons and excited state atoms, molecules and ions, may be responsible for the formation of the ionized species. It is then clear that flames may not be the best experimental medium to study the role played by the many individual chemical and physical processes that make up the total flame. For a better understanding of the flame chemistry, it is desirable to study these processes individually, preferably at room temperature.

The CHO^+ ions have also been observed in interstellar molecular clouds (Buhl and Snyder 1970, Herbst *et al* 1976, Duley and Williams 1984). There are two isomers of the CHO^+ ion with potential energy minima on the $(\text{H-C-O})^+$ surface (Woods *et al* 1975, Gudeman and Woods 1982). In the interstellar clouds, these isomers are believed to be produced due to the reactions: $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+$ (or HOC^+) + H_2 and $\text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+$ (or HOC^+) + H . The HCO^+ is produced in greater concentration and is known to be more stable than HOC^+ . Indeed, the number density of HCO^+ ions overwhelms HOC^+ ions by the ratio 94:6 in a given reaction involving the two isomers (Illies *et al* 1983, Redeker *et al* 1985). The ion-molecule reactions involving collisions of CHO^+ ions and CH_4 molecules have been studied at thermal energies. Adams *et al* (1978) observed no reaction byproducts and placed a limiting value on the total rate constant $k \leq 1 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, whereas Roche *et al* (1971) have observed $\text{CH}_5^+ + \text{CO}$ as the byproducts with a rate constant $k \leq 1 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In a recent study, Adams *et al* (1991) have studied the dissociative recombination $\text{CHO}^+ + e$ and have quantitatively determined the OH product distribution using laser fluorescence techniques. The total dissociative recombination rate coefficients for the $\text{CHO}^+ + e$ reaction have been measured by Leu *et al* (1973) at room temperature as well as at 205 K and are equal to $(3.3 \pm 0.5) \times 10^{-7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $(2.0 \pm 0.3) \times 10^{-7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The rate coefficient measured by Amano (1990) for the same process at 273 K is $3.1 \times 10^{-7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Based on the above description, it is clear that there is no information available on the electronically or vibrationally excited states of the byproduct species formed during collisions of CHO^+ ions and electrons or neutral species. In this communication, we wish to report our results on the electronic excitation of several species observed during collisions of CHO^+ and H^+ ions with O_2 , N_2 , H_2 and CH_4 molecules.

2. Experimental procedure

The experimental set-up used to collect data reported here has been described in detail elsewhere (Kushawaha and Michael 1988, 1989) and will not be repeated here. However, a brief description of the procedure used to collect the data will be given here. The projectile ions CHO^+ and H^+ were generated by electron impact with flowing methanol vapour and extracted through a small hole in the anode. The ions were then accelerated and passed through a magnetic mass selector and subsequently through a collision cell containing the desired target species. After passing through a collision cell, these ions were collected on a Faraday cup and measured by a sensitive electrometer. The target gas pressure was measured by a calibrated pressure gauge.

The light emitted from the collision cell due to the ion-molecule reaction inside the collision cell was viewed in a direction perpendicular to the ion beam. The light photons were dispersed by a 0.2 m scanning monochromator and detected by a cooled (-25°C) photomultiplier tube (PMT). The signal from the PMT was amplified and sent to a multichannel analyser for storage, analysis and subsequent plotting of the data.

The methanol used in the present study was purchased from the Fisher Scientific Co with a stated purity of 99% and was used without further purification. The H₂, N₂ and O₂ gases were purchased from Air-Products with a stated purity of 99.99% and used directly from the tank without purification.

3. Results and discussion

Electronic emission spectra from atomic hydrogen, i.e. H_β, H_γ and H_δ lines, CH and OH radicals and CH⁺, N₂⁺ and CO⁺ ions, were observed and recorded in the wavelength range 580–240 nm during collisions involving CHO⁺ and H⁺ as projectile ions and CH₄, H₂, and N₂ molecules as target species. The intensities of the atomic and molecular features were observed to be different at different laboratory kinetic energies of the projectile ions. The emission spectra were recorded only in the laboratory kinetic energy range of 100–900 eV. At kinetic energies lower than 100 eV, the ion current was too small and the spectra were too weak for calculating emission cross sections and a meaningful interpretation of the data was not possible. No attempt was made to record the emission spectra above the laboratory kinetic energy of 900 eV, mainly because of experimental limitations. During the collisions of CHO⁺ ions with CH₄ molecules, strong emission from the electronically excited states of CH radicals, i.e. CH (A²Δ-X²Π) and CH(B²Σ⁻-X²Π), OH radicals due to the transition (A²Σ⁺-X²Π), and CH⁺ and CO⁺ ions due to transitions CH⁺ (A¹Π-X¹Σ⁺) and CO⁺(B²Σ⁺-X²Σ⁺), respectively, and atomic lines of hydrogen were observed. The intensity of the Q-head of the (0, 0) band due to the transition CH(A²Δ-X²Π) was observed to be the strongest compared with the other band head due to this transition or other emission features observed due to CHO⁺ and CH₄ reactions under given experimental conditions. When CH₄ molecules were replaced by N₂ molecules, strong emission was observed from the (0, 0), (1, 0) and (2, 0) band heads due to the transition N₂⁺ (B²Σ⁺-X²Σ⁺) as compared with the CH(B²Δ-X²Π) and OH (A²Σ⁺-X²Π) radicals. Atomic lines of hydrogen were completely absent in this reaction. The emission due to the CH⁺ ions was either not present in the spectrum or it was completely overlapped by the strong (0, 1) band head of the N₂⁺ ion due to the transition (B²Σ⁺-X²Σ⁺). The same trend continued in the kinetic energy range of 100–900 eV at a particular pressure of the N₂ gas. With either CH₄ or N₂ molecules and the CHO⁺ ion, no emission spectrum due to CO molecules was observed at higher kinetic energies of the projectile ions, i.e. higher than 500 eV. However, at kinetic energies below 500 eV, a very weak emission spectrum, probably due to CO molecules, was observed in the wavelength range 570–480 nm. No electronic emission, atomic or molecular, was observed when H₂ or O₂ gas was substituted for CH₄ or N₂ gas and the experiments were performed with CHO⁺ ions in the laboratory kinetic energy range 100–900 eV. When CHO⁺ ions were replaced by H⁺ ions and reactions were studied with CH₄ molecules as target gas, strong emission lines of hydrogen atoms and emission bands due to CH radicals and CH⁺ ions were observed. The emission bands due to the OH radical transition (A²Σ⁺-X²Π) was also observed as an impurity. In figure 1, we display the emission spectra observed due to collisions of CHO⁺ and H⁺ ions with CH₄ and N₂ molecules at a laboratory kinetic energy of 900 eV. The emission bands denoted by I in figure 1 (upper scan) are probably due to N₂⁺ as an impurity. These peaks may be compared to the (1, 0) and (2, 0) bands due to the N₂⁺ band heads observed during the collisions of CHO⁺ ions and N₂ molecules shown in the middle scan of figure 1. The band head

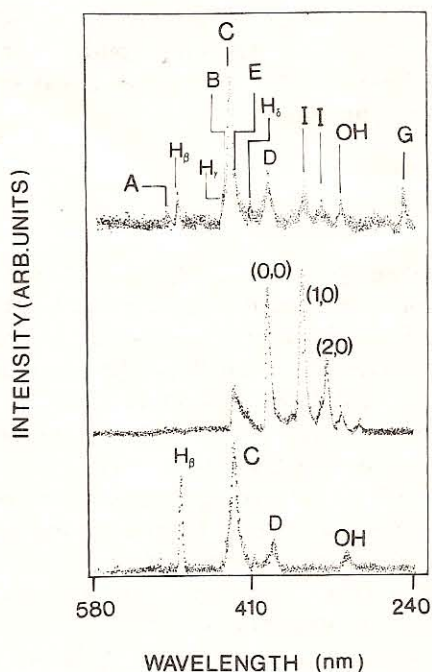
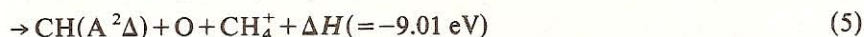
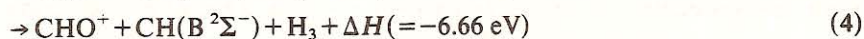
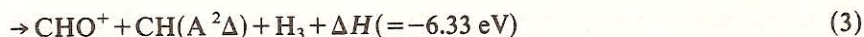
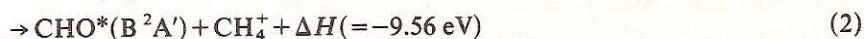
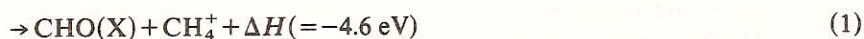
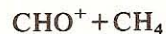
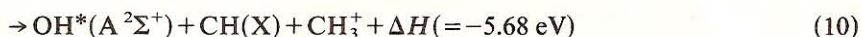
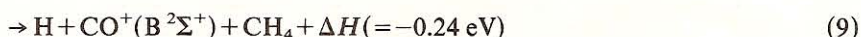
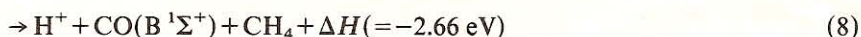
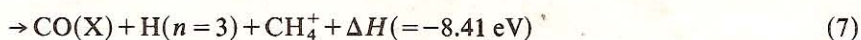
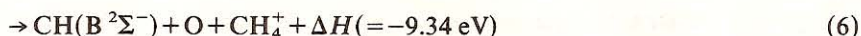


Figure 1. Electronic emission spectra observed due to collisions of various ions and molecules at a laboratory kinetic energy of 900 eV and CH_4/N_2 pressure of 4 mTorr. The spectra are not corrected for the optical detection efficiency. Upper scan, $\text{CHO}^+ + \text{CH}_4$; middle scan, $\text{CHO}^+ + \text{N}_2$; bottom scan, $\text{H}^+ + \text{CH}_4$. H_β , H_γ and H_δ are the atomic hydrogen lines at 486 nm, 434 nm and 410 nm, respectively. The (0, 0), (1, 0) and (2, 0) are the band heads due to N_2^+ ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$) transition. A, P-head of the (0, 1) band of the $\text{CH}(\text{A}^2\Delta - \text{X}^2\Pi)$ transition; B, Q-head of the (2, 2) band of the $\text{CH}(\text{A}^2\Delta - \text{X}^2\Pi)$ transition; C, Q-head of the (0, 0) band of the $\text{CH}(\text{A}^2\Delta - \text{X}^2\Pi)$ transition; D, Q-head of the (0, 0) band of the $\text{CH}(\text{B}^2\Sigma^- - \text{X}^2\Pi)$ transition; E, R-head of the (0, 0) band of the $\text{CH}^+(\text{A}^1\Pi - \text{X}^1\Sigma^+)$ transition; G, CO^+ band due to the transition ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$) transition; OH, R₁-head of the OH-radical due to the ($\text{A}^2\Sigma^+ - \text{X}^2\Pi$) transition.

due to the $\text{CH}(\text{B}^2\Sigma^- - \text{X}^2\Pi)$ transition and denoted by D in the upper scan of this figure may be slightly overlapped by the (0, 0) band head of N_2^+ as shown in the middle scan. The spectrum due to the collision $\text{H}^+ + \text{CH}_4$ is shown as the lowest scan in figure 1 and is free from any N_2^+ band structure. The assignments of these band heads are from Pearse and Gaydon (1976).

There are two processes which may be responsible for the observation of excited state atomic and molecular emission described above. These processes include collision-induced dissociative charge transfer and excitation processes. For the $\text{CHO}^+ + \text{CH}_4$ collisions, these processes may be written as follows:





where (X) or (*) are the ground or excited state species and ΔH is the exothermicity or endothermicity of the reaction. Here $\Delta H > 0$ means the reaction is exothermic. The ΔH values for the above processes were calculated by using the ionization (I), dissociation (D) and electronic excitation (E) energies of the various species involved in reactions (1)–(10). The ionization potentials (I) are $I(\text{CH}) = 10.6 \text{ eV}$, $I(\text{CH}_4) = 12.70 \text{ eV}$, $I(\text{CHO}) = 8.1 \text{ eV}$, $I(\text{CO}) = 14.01 \text{ eV}$, and $I(\text{CH}_3) = 9.8 \text{ eV}$, the dissociation energies are $D(\text{CH}) = 3.46 \text{ eV}$, $D(\text{CH}^+) = 4.08 \text{ eV}$, $D(\text{CO}) = 11.09 \text{ eV}$, $D(\text{H-CO}) = 1.54 - 1.0 \text{ eV}$ and the excitation energies are $E(\text{CH}, \text{A } ^2\Delta) = 2.87 \text{ eV}$, $E(\text{CH}, \text{B } ^2\Sigma^-) = 3.2 \text{ eV}$, $E(\text{OH}, \text{A } ^2\Sigma^+) = 4.01 \text{ eV}$, $E(\text{CO}, \text{B } ^1\Sigma^+) = 13.2 \text{ eV}$, $E(\text{CO}^+, \text{B } ^2\Sigma^+) = 4.95 \text{ eV}$ and $E(\text{CHO}^*, \text{B } ^2\text{A}') = 4.96 \text{ eV}$. The excitation and dissociation energy values were taken from Huber and Herzberg (1979) and the ionization potential energies were taken from Rosenstock *et al* (1977), except $I(\text{CHO})$, which was taken from Dyke (1987). Based on the ΔH values calculated using the value of $I(\text{CHO}) = 8.1 \text{ eV}$, as noted above, most of the processes are highly endothermic, except reaction (9) which is slightly endothermic. Observation of the various highly excited state species clearly indicates that for the endothermic processes to occur some other mechanism(s), completely different from the exothermic processes, is involved for the electronic excitation of these species. The most likely mechanism may be the conversion of the translational energy of the ions into internal energy of the byproduct species. Such a conversion of energy has been observed by us and others in the past for similar ion-molecule reactions for which the endothermicity was more than 6 eV (Kushawaha and Michael 1988, 1989, Kelley *et al* 1978). A set of similar reaction sequences may be written to explain the observation of the electronically excited state species involving collisions of H^+ ions and CH_4 or N_2 molecules. At this point, it may be worth noting that the reactions involving CHO^+ and H_2 or O_2 are highly endothermic and produce no emission. It may be possible that conversion of the translation energy into internal energy of the product species did occur but only a small number of excited state species were produced, leading to very weak emitted radiation from the excited state which could not be detected by our detection system.

The emission cross sections of the electronically excited state species was calculated by using the following expression (Kushawaha and Michael 1988, 1989):

$$\sigma = I_s / I_p n L.$$

Here σ is the emission cross section in cm^2 , I_s is the photon counts per second corrected for the detection efficiency of the optical system that included the solid angle of light collection, I_p the number of ions per second participating in the collision process inside the collision cell, n the number density of the target species in cm^3 and L (in cm) is the interaction length of the ion beam and the target gases inside the collision cell. By using the appropriate information in the above expression, we have calculated the emission cross section of the most intense atomic lines or molecular bands observed due to various emitters described above. The results of these calculations are reported in tables 1–3 for H_β , $\text{CH}(\text{A } ^2\Delta - \text{X } ^2\Pi)$ and $\text{CH}(\text{B } ^2\Sigma^- - \text{X } ^2\Pi)$ emitters in the laboratory

Table 1. Emission cross sections of atomic hydrogen line H_{β} , CH radicals in the excited states $CH(A) = CH(A^2\Delta-X^2\Pi)$ and $CH(B) = CH(B^2\Sigma^-X^2\Pi)$ observed during the collisions of CHO^+ ions and CH_4 molecules (4 mTorr) in the laboratory kinetic energy range 100–900 eV.

Kinetic energy (eV)	Cross section (10^{-20} cm^2)	
	H_{β}	CH(A)
900	0.2	1.02
750	0.8	3.70
650	1.24	6.32
550	0.76	5.62
450	0.12	8.70
300	—	4.40
100	—	2.74

Table 2. Emission cross sections of atomic hydrogen line H_{β} , CH radicals in the excited states: $CH(A) = CH(A^2\Delta-X^2\Pi)$ and $CH(B) = CH(B^2\Sigma^-X^2\Pi)$, observed during the collisions of H^+ ions and CH_4 molecules (4 mTorr) in the laboratory kinetic energy range 100–900 eV.

Kinetic energy (eV)	Cross section (10^{-20} cm^2)		
	H_{β}	CH(A)	CH(B)
900	2.0	1.6	0.35
750	4.6	4.4	0.38
650	5.8	6.5	0.95
550	7.2	6.8	0.90
450	8.2	8.3	1.87
300	7.5	8.7	0.70
100	4.2	2.0	0.40

Table 3. Emission cross sections of CH radicals $CH(A) = CH(A^2\Delta-X^2\Pi)$ and (0, 0), (1, 0) and (2, 0) band heads of $N_2^+ (B^2\Sigma^+-X^2\Sigma^+)$ transition observed during the collisions of CHO^+ ions and N_2 molecules (4 mTorr) in the laboratory kinetic energy range 100–900 eV.

Kinetic energy (eV)	Cross section (10^{-20} cm^2)			
	CH(A)	(0, 0)	(1, 0)	(2, 0)
900	0.25	1.30	1.69	0.50
700	—	3.60	5.50	0.35
500	0.36	2.86	3.80	0.18
300	0.2	1.30	1.40	0.1
100	—	0.67	1.00	—

kinetic range 100–900 eV. It is to be pointed out here that the cross section for the formation of CH(B) radicals due to collisions of $\text{CHO}^+ + \text{CH}_4$ cannot be measured reliably due to possible overlap by the (0, 0) band head of the N_2^+ (B–X) system (see figure 1) which may be present as an impurity. These cross sections may be regarded as accurate to within an experimental uncertainty of $\pm 30\%$. This estimate is based on the measured emission cross sections of atomic hydrogen lines observed due to collisions of He^+ and H_2 in our laboratory and those measured by Isler and Nathan (1972). The two cross sections were in agreement to within $\pm 20\%$. This agreement gave us confidence in the procedure used to calibrate our detection system and in the detection efficiency that was used to calculate the values of I_s in the above expression. Other details of our calibration procedure are published elsewhere (Kushawaha and Mahmood 1987).

In conclusion, we have studied the ion–molecule reactions involving collisions of CHO^+ and H^+ ions with CH_4 , N_2 , O_2 and H_2 molecules in the laboratory kinetic energy range 100–900 eV. During the collisions, we have observed electronic emission due to CH and OH radicals, CH^+ , CO^+ and H_2^+ ions and atomic hydrogen lines. By using the integrated intensity of the strongest bands and atomic lines, we have calculated the emission cross sections in the laboratory kinetic energy range 100–900 eV. These cross sections may be useful in theoretical modelling of the interstellar chemical processes and a better understanding of the chemical/physical processes at work in an oxy–hydrocarbon flame.

Acknowledgments

The research work reported here was partially supported by the Army Research Office grant no DAA103-89-G-0099, Air Force (Wright Patterson) grant no F33615-90-C-2038, NASA grant no NAGW-2450, Howard University Faculty Research Grant and Collaborative Core Unit of the Graduate School of Arts and Sciences. We thank Mr E Jones and Mr Bill Pinkney for providing technical help in the shops and in the laboratory.

References

- Adams N G, Herd G R, Geoghegan M and Smith D 1991 *J. Chem. Phys.* **92** 4852
- Adams N G, Smith D and Grief D 1978 *Int. J. Mass Spectrom. Ion Phys.* **9** 405
- Amano T 1990 *J. Chem. Phys.* **92** 6492
- Bayes K D 1988 *Chem. Phys. Lett.* **152** 424
- Bowers M T 1986 *Gas Phase Ion Chemistry* (New York: Academic)
- Buhl D and Snyder L E 1970 *Nature* **228** 207
- Calcote H F 1981 *Combust. Flame* **42** 215
- Cool T A and Tjsses D 1984 *Chem. Phys. Lett.* **111** 82
- Duley W and Williams D 1984 *Interstellar Chemistry* (New York: Academic)
- Dyke J M 1987 *J. Chem. Soc. Faraday Trans. II* **83** 69
- Fontijn A 1985 *Gas Phase Chemiluminescence and Chemi-ionization* (Amsterdam: North-Holland)
- Franklin J L 1972 *Ion-Molecule Reactions* (New York: Plenum)
- Gudeman C S and Woods R C 1982 *Phys. Rev. Lett.* **48** 1344
- Herbst E, Norbeck J M, Certain P R and Klemperer W 1976 *Astrophys. J.* **207** 110
- Huber K P and Herzberg G 1979 *Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold)
- Illies A J, Jarrold M F and Bowers M T 1983 *J. Am. Chem. Soc.* **105** 2562
- Isler R C and Nathan R D 1972 *Phys. Rev. A* **6** 1036

- Kelley J, Bearman G, Harris H and Leventhal J J 1978 *J. Chem. Phys.* **68** 3345
- Kushawaha V and Mahmood M 1987 *J. Appl. Phys.* **62** 2173
- Kushawaha V and Michael A 1988 *Chem. Phys.* **132** 373
— 1989 *Chem. Phys. Lett.* **154** 599
- Le Q N and Vanpee M 1985 *Combust. Flame* **62** 193
- Leu M, Biondi M and Johnsen R 1973 *Phys. Rev. A* **8** 413
- Miller W J 1976 *16th Int. Symp. on Combustion* (Pittsburgh, PA: The Combustion Institute) p 307
- Neils T, Brown J M and Evanson K M 1988 *J. Chem. Phys.* **88** 2087
- Pearse R W B and Gaydon A G 1976 *Identification of Molecular Spectra* (New York: Wiley)
- Peeters J and Vinckier C 1975 *15th Int. Symp. on Combustion* (Pittsburgh, PA: The Combustion Institute) p 969
- Phippen D E and Bayes K D 1989 *Chem. Phys. Lett.* **164** 625
- Redeker W W, Kemper P R Jarrold M F and Bowers M T 1985 *J. Chem. Phys.* **83** 1121
- Roche A E, Suttan M M, Bohme D K and Schiff H I 1971 *J. Chem. Phys.* **55** 5480
- Rosenstock H M, Draxl K, Steiner B W and Herron J T 1977 *J. Phys. Chem. Data* (suppl. no 1)
- Woods R C, Dixon T A, Saykally R J and Szanto P G 1975 *Phys. Rev. Lett.* **35** 1269