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Infrared absorption spectra of methylidene radicals in solid neon

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Infrared absorption lines of methylidene – $^{12}C^{1}H$, $^{13}C^{1}H$, and $^{12}C^{2}H$ – dispersed in solid neon at 3 K, recorded after photolysis of methane precursors with vacuum-ultraviolet light at 121.6 nm, serve as signatures of these trapped radicals.

Among many free radicals and other highly reactive neutral molecules and molecular ions of which infrared spectra have been reported in both gaseous and solid states, the methylidene radical is conspicuous by its absence. The infrared spectra of both gaseous $^{12}C^{1}H$ (ref. 1) and $^{12}C^{2}H$ (ref. 2) in vibrational–rotational transitions are well documented; spectra involving electronic transitions are long established, both experimentally and computationally.[3] Both $^{12}C^{1}H$ and $^{12}C^{2}H$ trapped in solid argon and krypton were identified in various electronic transitions in both absorption and emission.[4] Our experiments on the photolysis of methane dispersed in solid neon at 3 K have produced lines in infrared absorption spectra that have enabled us to characterize thereby this methylidene free radical, as we here report.

Gaseous mixtures of $^{12}C^{1}H_4$ or $^{13}C^{1}H_4$ or $^{12}C^{2}H_4$ with neon in proportions 1 : 100 to 1 : 10 000, or with added H_2 in proportions $CH_4 : H_2 : Ne = 1 : 6 : 1000$, were deposited for periods from 20 min to 26 h on a CsBr crystal maintained at 3 K in a refrigerator system (Janis RDK-415) mounted in the optical path of an interferometric spectrometer (Bomem DA8, spectral resolution 0.5 cm^{-1}, accuracy 0.1 cm^{-1} of reported wavenumbers) and irradiated with light of wave length selected in a range 120–165 nm from an undulator of a synchrotron (at National Synchrotron Radiation Research Center, Taiwan, beam line BL21 A2) for periods from 10 s to 510 min in total. The experimental setup is similar to that described previously.[5]

Difference spectra, as the absorbance curves before irradiation subtracted from the corresponding curves recorded after irradiation for varied periods, showed the production of new lines attributed to products of photolysis of the particular methane precursors. Spectral lines attributed to methylidene radicals of particular isotopic variants were observed, with signals due to other products identified according to their characteristic vibrational spectra; an analysis of the latter features will be presented elsewhere. Fig. 1 shows selected portions of the total spectra recorded between 2700 and 2780 cm^{-1} after irradiation

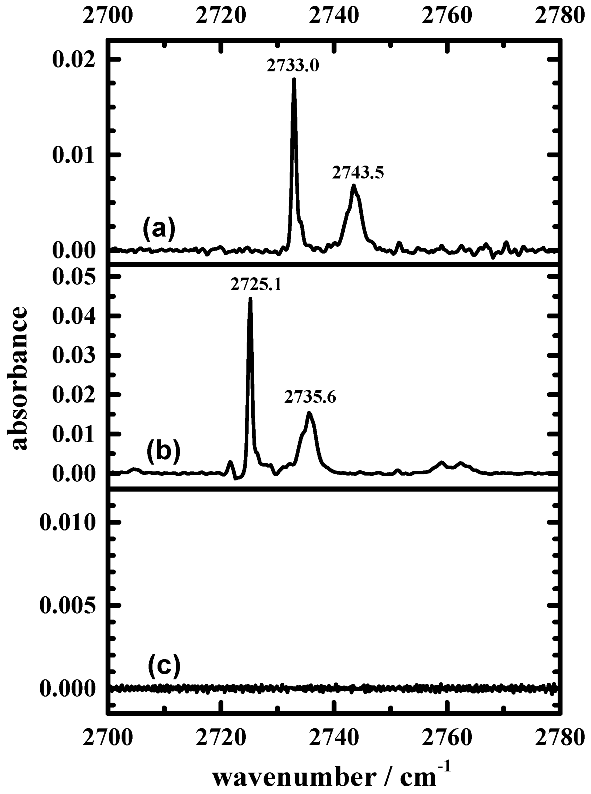

Fig. 1 Absorption spectra after irradiation of methane : H_2 : Ne = 1 : 6 : 1000 at 121.6 nm: (a) $^{12}C^{1}H_4 : {}^{1}H_2$: Ne for 450 min, (b) $^{13}C^{1}H_4 : {}^{1}H_2$: Ne for 510 min, (c) $^{12}C^{2}H_4 : {}^{1}H_2$: Ne for 510 min, all at 3 K; resolution 0.5 cm^{-1}, from 600 coadded interferograms.

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at 121.6 nm for samples (a) $^{12}C^1H_4:{}^1H_2:Ne = 1:6:1000$, (b) $^{13}C^1H_4:{}^1H_2:Ne = 1:6:1000$, and (c) $^{12}C^2H_4:{}^1H_2:Ne = 1:6:1000$; this spectral region includes the pertinent spectral lines of $^{12}C^1H$ and $^{13}C^1H$. As these lines occur in regions nearly free of interference of other carriers, their assignment is direct, according to the following analysis.

Upon photolysis of $^{12}C^1H_4$ in Ne or in Ne with a little added $^1H_2$, a line appears at 2733.0 cm^{-1}, detectable after irradiation for as little as 10 s, so indicating a primary photochemical product. The primary photochemical products of photolysis of gaseous methane that contain C are CH, CH_2 and CH_3 radicals.[6] The decreased rate of net production of CH after 10 min indicates that CH, like its precursor CH_4, is subject to photolysis or to reaction with other species produced in solid neon. The centre of the fundamental vibrational–rotational band of $^{12}C^1H$ in the gaseous phase is 2732.5 cm^{-1}.[1] This line at 2733.0 cm^{-1} is invariably accompanied with a weaker and broader line at 2743.5 cm^{-1}, with a constant ratio of net statures under all conditions; both lines are hence attributed to $^{12}C^1H$.

Upon photolysis of samples of $^{12}C^2H_4$ in Ne, a line at 2030.7 cm^{-1} is recorded, with a satellite line at 2041.0 cm^{-1}, as shown in Fig. 2. As the centre of the fundamental vibrational–rotational band of $^{12}C^2H$ in the gaseous phase is 2031.7 cm^{-1},[2] the two specified absorption signals are attributed to $^{12}C^2H$.

Likewise, upon photolysis of samples of $^{13}C^1H_4$ in Ne, a line at 2725.1 cm^{-1} with a satellite line at 2735.6 cm^{-1} is attributed to $^{13}C^1H$, as shown in Fig. 1(b). In this case there is no datum for the gaseous phase, but the ratio, 0.9971, of wavenumbers between the observed main lines of $^{13}C^1H$ and $^{12}C^1H$ is exactly the theoretical ratio, 0.9970, within experimental uncertainty.

Shifts of wavenumber between infrared transitions of molecules in the gaseous phase and the same transitions of the species dispersed in solid neon are generally less than 3 cm^{-1}. In regard to the possibility of alternative assignments, the barren spectral region near 2730 cm^{-1} is associated with few fundamental vibrational modes or intense vibrational transitions of other species; other primary photochemical products of methane, *i.e.* CH_2 and CH_3 radicals, are known to absorb at other wavenumbers in this region, greater than 2800 cm^{-1}. On this basis the assignment of the specified lines to their respective methylidene radical carriers is unequivocal.

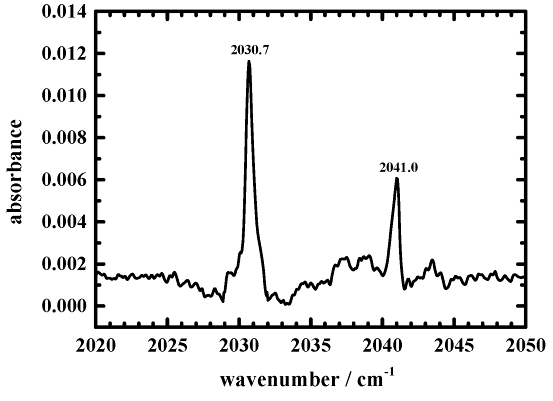

Fig. 2 Absorption spectrum after irradiation of $^{12}C^2H_4:{}^1H_2:Ne = 1:6:1000$ at 121.6 nm for 510 min, at 3 K; resolution 0.5 cm^{-1}, from 600 coadded interferograms.

For methylidene in each isotopic variant, the spectral signature that we observed comprises two separate features. The lines of $^{12}C^1H$ at 2743.5 cm^{-1} and of $^{13}C^1H$ at 2735.6 cm^{-1}, weaker than their respective adjacent main lines that have practically the same wavenumbers as the gaseous band centres, both appear to have a composite structure, unresolved under our spectral conditions. Whether the weaker line of $^{12}C^2H$ at 2041.0 cm^{-1} has a similar nature is difficult to ascertain: absorption of the C_3 radical, which has no deuterium isotopic effect, overlaps only that line, not significantly with the main line at 2030.7 cm^{-1}; the curve presented in the figure was derived by spectral subtraction of the C_3 signals. The intensity ratios between the satellite lines and the main lines are common to all three isotopic species. The cause of the doublet pattern of each isotopic species is difficult to explain. The wavenumber difference, (10.4 ± 0.1) cm^{-1}, between the components is constant for all three isotopic variants. As the principal rotational parameter of gaseous $^{12}C^1H$ is about twice the corresponding value for $^{12}C^2H$,[1,2] clearly a nearly free rotational motion is excluded. Although evidence for the rotation of OH and OD in solid neon at 4.2 K was claimed on the basis of electronic spectra,[7] our definitive spectra of hydroxyl radicals in solid argon at 12 K,[8] which is expected to be more amenable to rotational motion than solid neon at 4.2 K, provided no indication of such motion.

Likewise for imidogen radicals, electronic spectra of NH and ND in solid argon, krypton and xenon[9] were claimed to indicate the rotational motion of those radicals in their respective environments, but three lines in subsequent infrared spectra of NH in Xe were attributed instead to multiple sites in the lattice.[10] Single absorption lines of imidogen radicals as three isotopic variants in solid argon at 20 K (ref. 11) provided no evidence for rotational motion. By dint of the similarity of structures of CH, NH and OH radicals and of their spectra, we conclude that the doublet nature of the absorption patterns of CH in three isotopic variants is not due to the free rotational motion of these free radicals within their lattice sites in solid neon. An alternative cause of the doublet nature is likely some site effect in the neon lattice, but we have no direct evidence of such a cause or the particular geometric details.

Infrared absorption lines of methylidene radicals dispersed in solid neon at 3 K were recorded after photolysis of methane precursors with vacuum-ultraviolet light. These specified infrared absorptions will serve as spectral signatures to enable the identification of this trapped radical in other experiments.

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