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RADIATIVE DECAY OF VIBRATIONALLY EXCITED CH_2^-

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Abstract—We have observed the presence of vibrationally excited CH_2^- created in a discharge, by measuring the photodetachment from CH_2^- as it radiatively relaxes in a high vacuum ion trap. We used a tunable IR laser to produce photons with energies above and below the expected threshold for removing an electron from the ground state. The time dependence of the photodetachment is consistent with the electron affinity of 5250 cm^{-1} (0.65 eV) obtained by Sears and Bunker for the ground state $\tilde{X}^3B_1$ methylene. We have tentatively assigned radiative lifetimes for the excited bending vibrations of CH_2^-: 600 ± 300 msec for $v_2 = 1$, 80 ± 40 msec for $v_2 = 2$, and 10 ± 5 msec for $v_2 = 3$.

INTRODUCTION

Hot bands are a potential problem in threshold measurements made by photoelectron and photodetachment spectroscopy of negative ions.[1,2] The difficulty in creating a sufficient current of negative ions often forces experimentalists to use discharge, sputter and other high temperature ion sources. A large fraction of the ions produced in these sources may be in vibrationally excited states, and the task is to identify the signal arising from these states. Normally, the intensity of these hot bands can be altered by changes in sources, precursor gases and extraction voltage, which affect the vibrational temperature. Frequency shifts from isotopic substitution can also help to assign hot bands. While these methods are usually sufficient, in the case of the photoelectron spectrum of methylene such an analysis failed to correctly establish the presence of hot bands.

The ground $\tilde{X}^2B_1$ state of the anion CH_2^- is similar in geometry to the $\tilde{a}^1A_1$ of the neutral, because the extra electron is in a non-bonding $1b_1$ orbital perpendicular to the plane of the molecule. As a result, detachment occurs primarily by bending transitions with $\Delta v_2 = 0$. This has been observed in the photoelectron spectrum[3,4] as a single large peak and in the photodetachment spectrum[5] as a sharp threshold. In photodetachment to the ground $\tilde{X}^3B_1$ state of CH_2, an electron in a slightly bonding $3a_1$ orbital is removed. There is a significant change in bond angle from 102.7° to 133.8° and in the energy of the linear configuration, from 11,500 cm^{-1} to 1938 cm^{-1}. The poor Franck–Condon factors for the $\Delta v_2 = 0$ bending transitions result in an extended vibrational progression above threshold, making it difficult to distinguish the true origin from the hot bands, which are weak steps below threshold.

Engelking *et al.*[4] concluded that no hot bands were present in the photoelectron spectrum of CH_2^-. They placed the threshold for detachment to the ground $\tilde{X}^3B_1$ state at the origin of the observed vibrational progression. The resulting electron affinity of 1630 cm^{-1} for the ground state $\tilde{X}^3B_1$ (0.210 eV) led to a controversial value of $T_0 = 5600\ cm^{-1}$ (0.68 eV or 19.5 kcal mol^{-1}) for the $\tilde{a}^1A_1$ state of CH_2. The weight of experimental and theoretical work on methylene contradicts this result, and the most recent results[6] give a value of 3165 ± 20 cm^{-1} (0.392 ± 0.003 eV or 9.1 kcal mol^{-1}) for the splitting between the singlet and triplet states (Shavitt[7] has given an excellent review of the controversy over the singlet–triplet gap). A correct simulation[8] based on accurate spectroscopic constants fits the photoelectron spectrum with an electron affinity of 5250 ± 160 cm^{-1} (0.65 ± 0.02 eV) and a vibrational temperature of 2500 K. The evidence now indicates that three (or possibly four) hot bands were present in the photoelectron spectrum, as was first suggested by Harding and Goddard[9] based on their *ab initio* GVB calculations. Very recently, using an improved photoelectron spectrometer, Lineberger[10] was able to obtain a spectrum of vibrationally cool CH_2^- formed in a flowing afterglow source. These new results confirm the expected value for the electron affinity.

In this note, we shall describe an experiment in which we measured the time dependence of photodetachment from CH_2^- at frequencies near threshold. By allowing the ions to cool radiatively in a trap for times up to 0.5 sec before photodetachment, we have directly observed the existence of vibrationally excited states of CH_2^- formed in a discharge. From the decays, we have tentatively assigned lifetimes for these states.

EXPERIMENTAL

Our approach is to store the CH_2^- in a high vacuum ion trap and then to probe the radiative decay of vibrationally excited ions at various storage times by measuring the photodetachment signal, using photons of energy above and below the electron affinity. To obtain the decay rates, we increment the trap residence time and measure the photodetachment at each step. In our experiment, we observe the depletion of the parent anion population caused by photodetachment with IR light. The signal is thus the sum over all energetically allowed transitions. At photon energies immediately above the electron affinity, all vibrational states can be photodetached, although the ground vibrational state can only detach by a $\Delta v_2 = 0$ transition. Due to the poor Franck–Condon factors, one expects a weak contribution from $v_2'' = 0$ despite its large population. Because the higher bending states have a larger cross section, one expects a decay of the photodetachment

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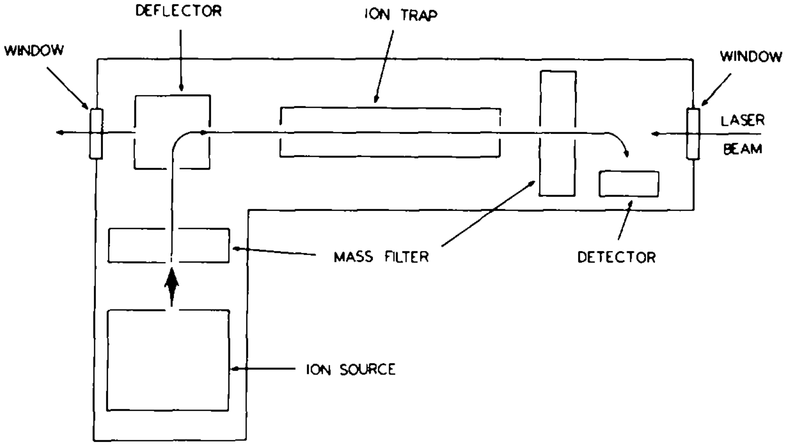

Fig. 1. Schematic of molecular ion spectrometer. The ion source is a duoplasmatron. The first mass filter is a 60° sector magnet and the second is a quadrupole mass spectrometer. The deflector is an electrostatic quadrupole. The ion trap is a 0.5 m radio frequency octupole ion guide.

signal to a constant level as the vibrationally excited CH_2^- relax. Below threshold, only the vibrationally excited states are photodetached. As we trap the ions for longer times, signals from the excited states will disappear, and the photodetachment should decrease to the ground state intensity for each frequency.

A 1–2 msec pulse of CH_2^- from a mass spectrometer is injected into a 0.5 m long ion trap (Fig. 1 is a block diagram of the machine). The ions are stored for some variable duration, after which a tunable IR laser is fired into the trap. The ions are released, mass analyzed, and counted. The same cycle is repeated without the laser, to measure the background count rate. After summing over many cycles, the difference gives the average depletion caused by photodetachment. The experiment is performed by measuring the depletion while varying the trapping time at a fixed laser frequency. After normalizing to the background, the signal is independent of the time dependent trapping efficiency, low frequency plasma fluctuations and other noise not correlated with the laser.

The CH_2^- are created by a hot cathode duoplasmatron, in a discharge of 60–300 mTorr of methane, with an emission current of about 1 mA. The ions are accelerated to 360 eV and mass analyzed by a 60° sector magnet. The ion beam enters the ultra-high vacuum region where it is bent 90° by an electrostatic quadrupole deflection field[11] into an axis collinear with the laser beam and decelerated to 1 eV.

The ions are trapped inside a radio frequency octupole ion guide based on the design of Teloy and Gerlich.[12,13] It consists of eight molybdenum rods, 50 cm long and 3 mm in dia., positioned symmetrically on a 12.5 mm dia. circle. Approximately 150 V of radio frequency are applied to the octupole rods, creating an effective potential that traps the ions transverse to the axis of the guide. By raising the potential of the lens elements at the entrance and exit of the ion guide, these elements act as electrostatic mirrors and the ions are confined within the trap. The ions are pulsed into the trap by lowering the voltage of the entrance lens element for 1–2 msec. After a computer-generated delay, the ions are released through the exit lens. The pressure in the trap region is typically below 5×10^{-9} Torr. Collisions within the trap become important for times greater than 1 sec.

Table 1. Radiative lifetimes of bending states of X^2B_1 CH_2^- and a^1A_1 CH_2

v_2	Anion $\tilde{X}^2B_1$ experimental lifetime (msec)	Neutral[a] $\tilde{a}^1A_1$ theoretical lifetime[b] (msec)
1	600 ± 300	950
2	80 ± 40	290
3	10 ± 5	140

[a] $K' = K'' = 0$ transitions.

[b] These results are obtained from *ab initio* CI calculations of the dipole moment function, integrated over semi-rigid bender vibrational wavefunctions.[15]

The laser beam is collinear with the axis of the trap, and passes completely through the machine, entering and exiting through two sapphire windows. This arrangement minimizes light scattering and reduces problems due to desorption or photoionization as the light strikes surfaces in the machine. No depletion was observed using ions with higher thresholds; hence, no laser correlated noise was evident.

Tunable IR radiation is generated by an optical parametric oscillator (OPO) similar to that developed by Brosnan and Byer.[14] A $LiNbO_3$ crystal in a resonant cavity is pumped in the far field of a Quanta Ray Nd:YAG laser at 1.06 μm. For frequencies from 5000 cm^{-1} to 7000 cm^{-1}, it produces 10 nsec pulses of 8–12 mJ at a 10 Hz repetition rate. There is no grating in the cavity, so the linewidths are typically 4–10 cm^{-1}, sufficient for the current experiment. The linewidth and divergence are anomalously large near 4700 cm^{-1}, where the two frequencies created by the OPO become degenerate. At degeneracy, the linewidth is about 200 cm^{-1} FWHM, the energy 13–16 mJ per pulse.

RESULTS AND DISCUSSION

The time dependence of the photodetachment was taken at three frequencies: 4700 cm^{-1}, 5690 cm^{-1} and 6320 cm^{-1}. Photodetachment at 4700 cm^{-1} is below the expected threshold of 5250 cm^{-1} (0.65 eV). Three time ranges were scanned: 1 msec to 37 msec, 1 msec to 153 msec (at 4700 cm^{-1} only) and 1 msec to 501 msec.

The decay curves taken with photon energies above threshold are shown in Fig. 2. These curves are normalized to unity at $t = 1$ msec. At both 5690 cm^{-1} and 6320 cm^{-1}, the signal decreases by about a factor of two within the first 200 msec, but then remains almost constant for times up to 500 msec. If we assume that the ions have almost cooled by 500 msec, then the photodetachment at that time will arise primarily from the ground vibrational state. The decay curve at 4700 cm^{-1}, shown in Fig. 3, is qualitatively different; the photodetachment signal has decreased by an order

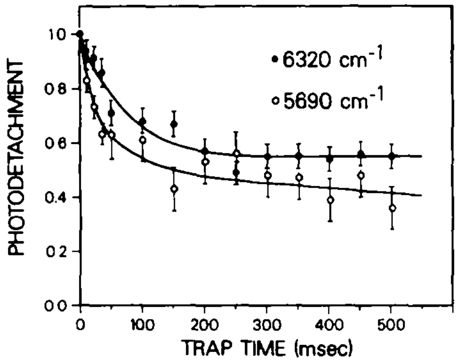

Fig. 2. Photodetachment signal from CH_2^- as a function of trapping time, normalized to unity at $t = 1$ msec. Laser frequencies are above the detachment threshold at 6320 cm^{-1} and 5690 cm^{-1}.

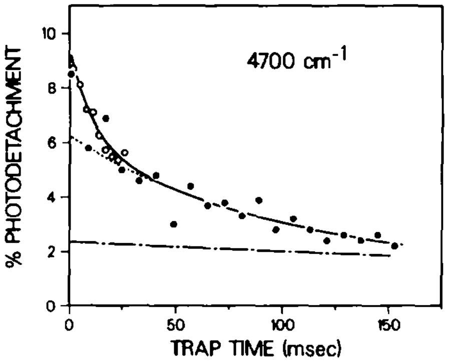

Fig. 4. Per cent photodetachment from CH_2^- as a function of trapping time with laser frequency at 4700 cm^{-1}, showing short time detail of Fig. 3. ——, fit to sum of three exponentials; — — —, fit to the $v = 1$ decay; - - - -, fit to the sum of $v = 1$ and $v = 2$ decays. Data from a 1 to 29 msec scan are shown in open circles.

of magnitude at 500 msec. These observations clearly demonstrate the presence of hot bands, and suggest that the electron affinity of ground state CH_2 is bounded by 4700 cm^{-1} and 5690 cm^{-1}, in agreement with the previous results.[7,9]

We have tentatively fit the decay at 4700 cm^{-1} to a sum of exponentials; three decay rates were needed in order to fit the data. The fit at shorter times can be seen in more detail in Fig. 4, and the lifetimes are given in Table 1. Fitting to multiple exponentials can be difficult; very similar decay rates would appear as a single decay. In our case, however, the observed rates all differ by a factor of four or more. The poor signal to noise does degrade the accuracy of the lifetime measurements, but the data still requires a minimum of three rates. The most serious problem is at long times, where the weak signal and the low duty cycle make it difficult to obtain good signal to noise. We cannot rule out, on the basis of the data alone, the possibility of a small signal that does not decay with time.

To check whether the observed photodetachment is due entirely to single photon excitation, we measured the power dependence at 4700 cm^{-1}, shown in Fig. 5. The power dependence at 1 msec delay gives evidence for at least three populations of absorbers, two of them saturated at full power. The power dependence after a 30 msec delay indicates that the strongest absorber, i.e. the one that saturates at the lowest power, has disappeared within 30 msec. We do not see evidence for two photon effects.

The analysis of the data at 4700 cm^{-1} gives us three decay rates from the time dependence and three populations from the power dependence. If we assume that the electron affinity is 5250 cm^{-1}, as predicted, then we would expect to see signals from three vibrational states. One further expects that $v_2 = 3$ would be the strongest absorber, because it can be photodetached at 4700 cm^{-1} by $\Delta v = 0, -1$ and -2 transitions to the neutral. The simplest model to explain the data would assign the longest lifetime to $v_2 = 1$, the intermediate to $v_2 = 2$ and the shortest to $v_2 = 3$.

Bunker and Langhoff[15] have recently done *ab initio* calculations for the dipole moments of neutral CH_2. Using the semi-rigid bender wavefunctions and the bending potential derived from spectroscopic data, they then calculated vibrational transition matrix elements. For illustrative purposes, we have listed in Table 1 the theoretical vibrational lifetimes ($K' = K'' = 0$) for the $\tilde{a}^1A_1$ state of the neutral. Note the trend of decreasing lifetime with increasing vibrational quan-

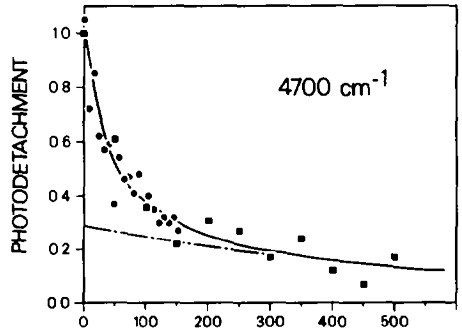

Fig. 3. Photodetachment from CH_2^- as a function of trapping time, normalized to unity at $t = 1$ msec. Laser frequency is below detachment threshold at 4700 cm^{-1}. ——, fit to sum of three exponentials; — - —, fit to the $v = 1$ decay. Data from a more accurate measurement from a 1 to 153 msec scan are shown in closed circles.

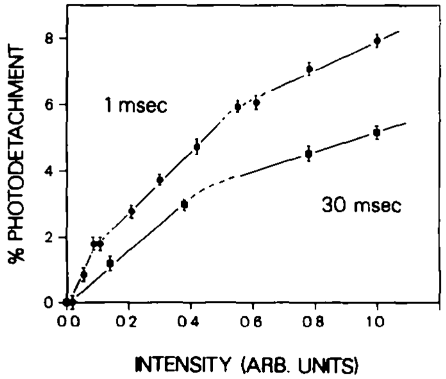

Fig. 5. Power dependence of CH_2^- photodetachment at 4700 cm^{-1}, taken at two trap times (●, 1 msec; ■, 30 msec). Intensity is in arbitrary units: full scale is approximately 5 MW cm^{-2} peak power over a 5 mm dia. spot for a 10 nsec pulse.

tum number. Our results show faster decays for the anion; furthermore, the lifetime of the excited anion decreases far more rapidly with v_2.

A simple calculation shows that the motion of the anion's charge with respect to the center of mass[16] in CH_2^- will add to the dipole moment and enhance the strength of the vibrational transitions. From this naive picture, one might expect the ion decays to be faster than the corresponding rates in the neutral singlet; of course, one must be very cautious in comparing the properties of the neutral to those of the anion. To better test our assignment, accurate calculations for the anion's dipole moment and vibrational lifetimes are currently being performed.

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