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Velocity-modulation infrared laser spectroscopy of molecular anions

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The velocity-modulation technique has been used with colour-centre lasers and diode lasers throughout the vibrational infrared region to measure high-resolution vibration–rotation spectra of fundamental anions.

INTRODUCTION

Although molecular anions are of fundamental significance in chemistry and in related disciplines, high-quality information on their structures, properties, and dynamics has been very difficult to obtain. Existing experimental knowledge of the structures and properties of negative ions comes principally from diffraction and low-resolution spectroscopy experiments carried out in condensed phases and from gas-phase electron detachment studies made in ion traps and ion beams. The latter techniques have been developed by Lineberger, Brauman and others into elegant and powerful tools for measuring electron affinities, energies and in some cases approximate geometries of negative ions and their associated neutral radicals. Nevertheless, because negative ions have not been amenable to absorption spectroscopy, there have been virtually no precise measurements of their molecular structures and potential functions. *Ab initio* theoretical calculations, which can be carried out with high accuracy for molecular cations, are more difficult for negatively charged molecules, and their reliability in this context is relatively untested.

Two complementary new experimental techniques for measuring high-resolution vibration–rotation spectra of negative ions have been developed in the last two years. Lineberger and his colleagues at the Joint Institute for Laboratory Astrophysics have perfected a laser electron detachment approach that they call 'vibrational autodetachment spectroscopy'; Neumark *et al.* (1985); in this technique a tunable infrared laser excites vibrational transitions in a beam of negative ions for which the electron binding energy is less than the energy of the laser photon. The excited vibrational state is thus 'quasibound' and autodetaches the extra electron on a time scale determined by the electron–nuclear coupling terms neglected in the Born–Oppenheimer approximation. This timescale varies over orders of magnitude with the quantum state of the anion, but is long enough to yield hyperfine-resolved vibration–rotation spectra, as well as important information on the dynamics of the autodetachment process. Neumark *et al.* (1985) have used this technique to carry out the first spectroscopic study of NH^-, which has been extended in recent work by Miller & Farley (1987) and Al-Za'al *et al.* (1986, 1987). Similar experiments have been carried out with visible lasers for $C_2H_3O^-$ (acetaldehyde enolate), CH_2CN^-, and FeO^-, in which states having the additional electron bound to the permanent dipole moment of the neutral molecule were observed (Read *et al.* 1984; Lykke *et al.* 1984; Anderson *et al.* 1987). It thus appears that autodetachment spectroscopy will be applicable to a large class of negative ions.

The most stable molecular anions have filled valence shells and are often the conjugate bases of common simple acids; these are the so called 'classical anions'. Some of the more ubiquitous examples are NO_3^- (nitrate), HSO_4^- (bisulphate), HCO_3^- (bicarbonate), NH_2^- (amide), CN^- (cyanide) and OH^- (hydroxide). The extra electrons in these species are quite strongly bound, often by 3 eV or more, and visible radiation is of insufficient energy to detach them. Hence, these very stable negative ions are actually quite difficult to study by the indirect ion-beam spectroscopy methods.

EXPERIMENTAL

A new laser absorption spectroscopy technique, developed recently at Berkeley for studying molecular ions in electrical discharges (Gudeman & Saykally 1984), is very well suited for measuring vibration–rotation spectra of the strongly bound 'classical anions'. In an electrical discharge plasma, Debye shielding of positive ions by the electrons allows a high concentration of charged species to exist; e.g. 0.01 Torr† of positive ions can be obtained in these plasmas. Hence, direct absorption spectroscopy can be used to study ions in plasmas; however, the concentration of neutral molecules in these media is still at least three orders of magnitude larger than that of the ions, and interference from the more abundant neutral absorbers would severely obscure the molecular-ion spectra under ordinary conditions.

The approach developed at Berkeley to separate absorption or emission features of ions from those of the more abundant neutral species has been to take advantage of the Doppler effect that results from the net drift motion of ions in the electric field of a positive column plasma. In a DC positive column plasma, an electric field develops along the axis of the discharge such that positive ions are accelerated toward the cathode and negative ions toward the anode. In the plasma cells used for this work this electric field is about 10 V cm^{-1}. Ions experiencing this field and making many collisions with neutral species before they are neutralised by electrons at the cell walls reach an average drift velocity (V_d), determined by the properties of these collisions, of *ca.* 500 m s^{-1}, which is about the same magnitude as the average random thermal velocity in the discharge. This net motion results in a Doppler shift in the spectra of ions, given by the usual first-order expression

$$\Delta\nu_{\text{Doppler}} = (V_d/C)\nu_{\text{IR}}.$$

The magnitude of this shift (*ca.* 10^{-6} of the infrared transition frequency) is about the same as the linewidth determined by the random thermal motion. By repeatedly reversing the polarity of the plasma we can essentially Doppler shift an absorption line into and out of resonance with a tunable monochromatic infrared laser. Because neutral species do not experience such Doppler effects in their spectra, rapid polarity switching (50000 times per second) and phase-sensitive detection of the laser power allows us to both achieve a very high absorption sensitivity (*ca.* 10^{-6}) while suppressing the absorptions of the more abundant neutral species by as much as 99.9%. This technique is termed 'velocity-modulation laser spectroscopy'.

Diagrams of the Berkeley velocity-modulation spectroscopy experiments are shown in figures 1 and 2. Tunable infrared laser radiation, either from a Burleigh colour-centre laser (2850–4200 cm^{-1}) or from a Laser Analytics lead-salt diode laser (350–3000 cm^{-1}) is directed through a velocity-modulation sample cell into a suitable detector. With the colour-centre system, the laser beam is split into two components, and one of them impinges on a matched reference

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† Torr ≈ 133.3 Pa.

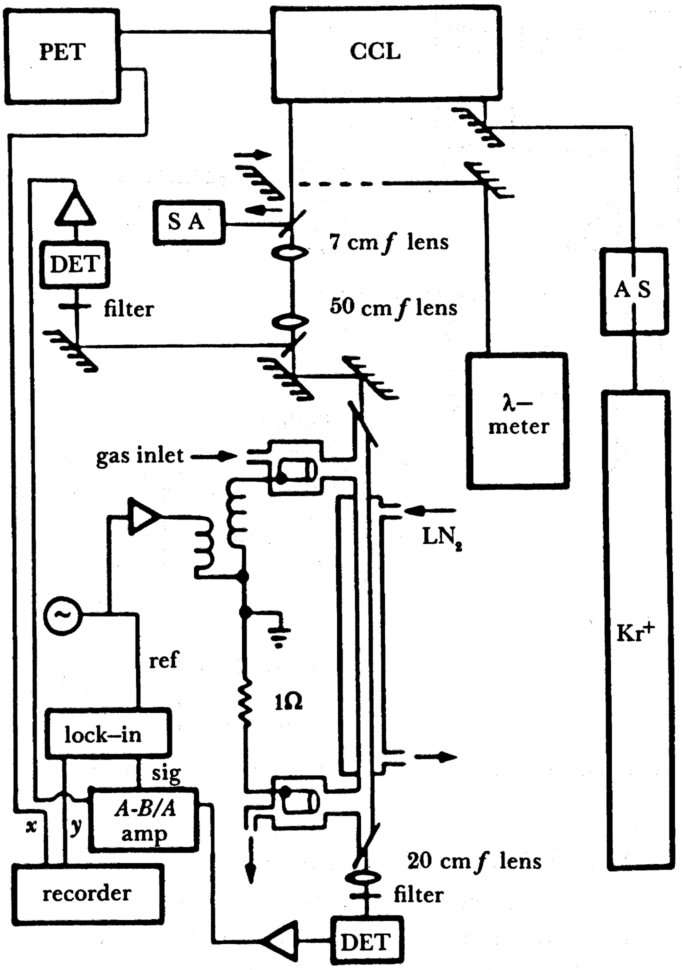

FIGURE 1. Diagram of the Berkeley colour-centre velocity-modulation laser spectrometer.

detector for subtraction of low-frequency amplitude fluctuations. The detector outputs are preamplified, subtracted in a difference amplifier, and demodulated at the discharge frequency to yield the velocity-modulation spectra, which have the usual first-derivative lineshape characteristic of frequency-modulation techniques. The laser frequency in these experiments is measured to high accuracy with either the lines from a calibration gas or with a wavemeter. A microcomputer controls the scanning of the laser and the collection of data. Both infrared laser systems are capable of measuring fractional absorptions as small as one part in a million with an accuracy limited by the Doppler linewidths (*ca.* 10^{-7}).

The velocity-modulation plasma cells are usually 1 cm × 100 cm, can be cooled to 77 K, and operate at pressures in the range 1–50 Torr. The ion density achieved when these plasmas are driven at 500 W is near 10^{14} ions cm^{-3}. Studies of the dynamics of positive ions have shown that rotational temperatures of ions are in equilibrium with the neutral gas kinetic temperature in the centre of the plasma, which is *ca.* 200 K hotter than the cell walls in He or H_2 plasmas because of finite thermal conductivity of the gas mixture.

Over the past several years we have employed the velocity-modulation technique in studies of infrared spectra of a variety of fundamental positive molecular ions (Gudeman & Saykally

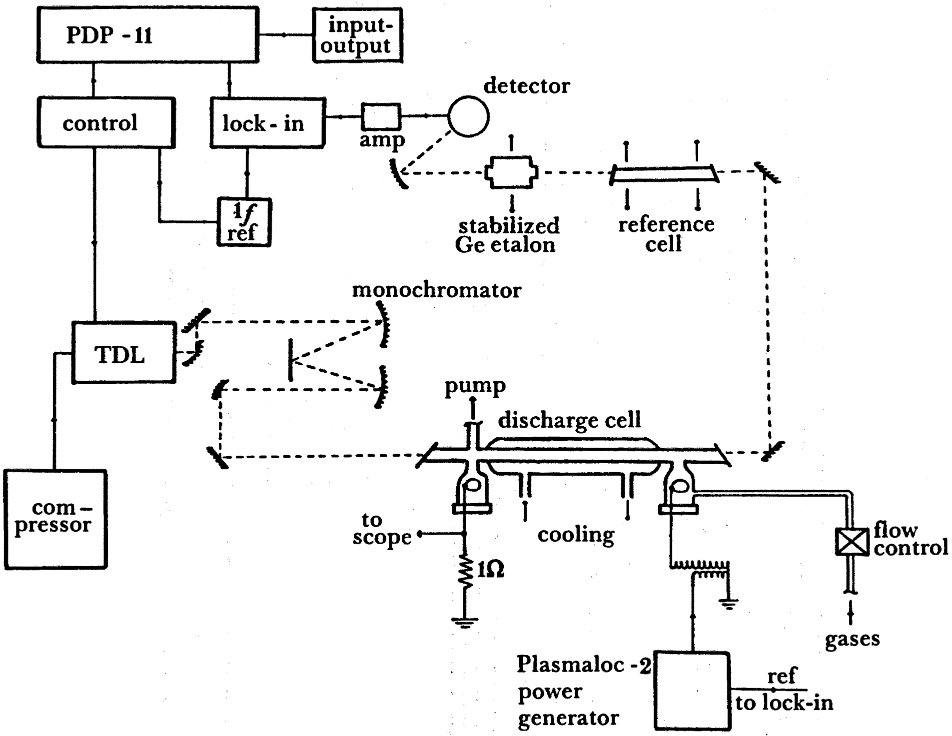

FIGURE 2. Diagram of the Berkeley diode laser velocity-modulation spectrometer.

1984), including H_3O^+, NH_4^+, HCO^+, HNN^+, HCS^+, CF^+, CCl^+, and H_2F^+. The goals of this work were to determine accurate molecular structures and potential functions near the equilibrium configurations, and to investigate the dynamics of charged particles in plasmas. Several other research groups have also used the velocity-modulation method for spectroscopic studies of important molecular cations; most notably, Oka's group at the University of Chicago has studied H_3^+, NH^+, NH_2^+, H_3O^+, H_2O^+, OH^+, NH_4^+, $HCNH^+$, CH_3^+ and possibly $H_3C_2^+$ (protonated acetylene) and Davies's group at Cambridge University has investigated H_3O^+, HCO^+, HCS^+, HCl^+, SH^+ and some other ions. Several other groups have very successfully used direct laser absorption spectroscopy of different types of plasmas (negative glows) for studies of interesting ions, but without this definitive discrimination against neutral molecules. Considering that the first observation of the infrared absorption spectrum of a molecular ion was made by Takeshi Oka as recently as 1980, the fact that more than 25 charged species have now been studied in detail by infrared spectroscopy indicates the tremendous rate of progress in this field (Gudeman & Saykally 1984).

In August 1985, Jeff Owrutsky, a graduate student at Berkeley, discovered the vibration–rotation spectrum of hydroxide in a H_2–O_2–Ar discharge (Owrutsky *et al.* 1985). In an interesting development, the OH^- signals disappeared when the cell was cleaned. It was later determined that the existence of a layer of sputtered metal on the discharge cell wall was necessary to achieve large negative-ion signals (Rosenbaum *et al.* 1986). This same effect was observed for NH_2^- in an NH_3 plasma. The actual role of the sputtered metal is presently unclear, but it may involve a surface-enhanced production of negative ions in these plasmas.

The magnitude of the metal enhancement effect is demonstrated in figure 3. This spectrum

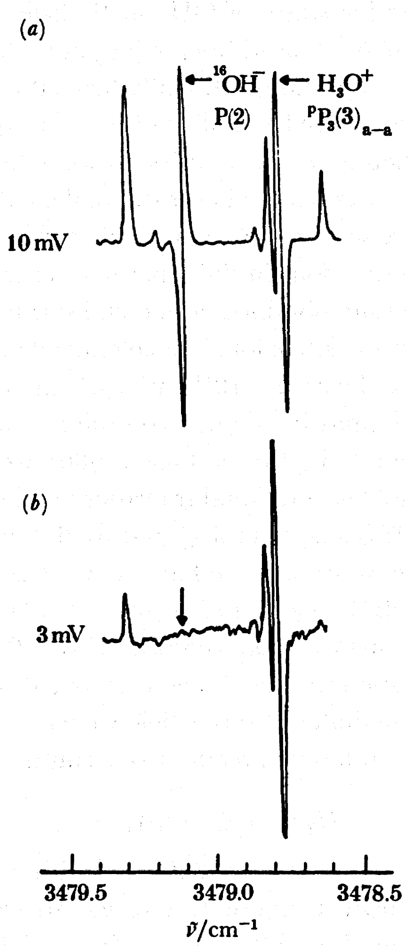

FIGURE 3. Comparison of the P(2) transitions of OH^- and the $^PP_3(3)_{a-a}$ transition of H_3O^+ observed in a clean discharge cell (*b*) with those observed in a cell with copper metal sputtered on the cell wall (*a*). Positive ion signals are not strongly affected by the condition of the cell walls.

also demonstrates two important features of the velocity-modulation technique. In this 1 cm^{-1} scan, both the incompletely suppressed absorption of a neutral molecule (highest-frequency line) and absorptions from positive ions (H_3O^+) appear, in addition to the OH^- lines. These absorptions are easily distinguished; the neutral features become very much larger (greater than 100) if detected at twice the discharge frequency ($2f$) because the plasma turns on and off at this rate, changing the concentrations of most species as it does. The effect cancels out if detection is carried out at the discharge frequency itself ($1f$) except for the residual population changes caused by the inability to make both half-cycles of the AC discharge exactly identical. Also, positive and negative ions exhibit opposite translational motions in the plasma electric field and, as a result, their demodulated first derivative lineshapes have opposite symmetry. Hence it is straightforward to decide whether or not a given absorption feature is caused by a negative or positive ion, or by a neutral species. This capability is an extremely important advantage of the velocity-modulation method, because the plasmas that optimize the concentrations of most negative ions also contain high densities of neutral molecules having strong and extensive infrared absorptions, and the positive ions generated in most plasmas are usually 100 times more abundant than the anions.

We have carried out an extensive study of OH^- at Berkeley, including both the ^{16}O and ^{18}O isotopes (Rosenbaum *et al.* 1986). The addition of argon to the H_2–O_2 plasma enhances the OH^- concentration substantially and also rotationally heats the ion. This enhancement of the OH^- density is the result of the reduced mobility of ions in argon relative to that found in lighter gases that forces a higher total ion density to exist for a given operating current. Rotational heating arises because argon has a lower thermal conductivity than do lighter gases. Based on these observations, there seem to be no dramatic differences between such dynamical properties of OH^- and small positive ions in these plasmas, except for the large enhancement (greater than 10^2) of the OH^- density obtained with metal sputtered on the cell walls, an effect that has never been observed for a positive ion. The average density of OH^- in H_2–O_2 plasma with argon added is calculated to be *ca.* 2×10^{11} cm^{-1}, which is lower than that observed for simple positive ions in similar plasmas by about two orders of magnitude.

Based on the results of this analysis, Liu & Oka (1986) were nearly able to assign two absorptions observed near 400 cm^{-1} to rotational transitions of OH^-. Guided by the theoretical calculations carried out by Lee & Schaefer (1985) and by Botschwina (1986) and by spectroscopic results from condensed phase studies, we have now made extensive studies of a variety of molecular anions, including NH_2^- (Tack *et al.* 1986 *a*, *b*), SH^- (Gruebele *et al.* 1987 *a*), N_3^- (Polak *et al.* 1987 *a*), NCO^-, (Gruebele *et al.* 1987 *b*), NCS^- (Polak *et al.* 1987 *b*) and CCH^- (Gruebele *et al.* 1987 *c*) by vibration–rotation spectroscopy, through the use of the velocity-modulation technique. In the remainder of this article we will very briefly describe the results of these studies. We encourage the interested reader to consult the original references for details.

Hydrosulphide (SH^-)

Representative spectra of SH^- observed near 2600 cm^{-1} with the Berkeley diode laser velocity modulation spectrometer are shown in figure 4. The signals were optimized in a discharge through a mixture of 70 mTorr of H_2S, 400 mTorr of H_2, and 700 mTorr of Ar with the cell

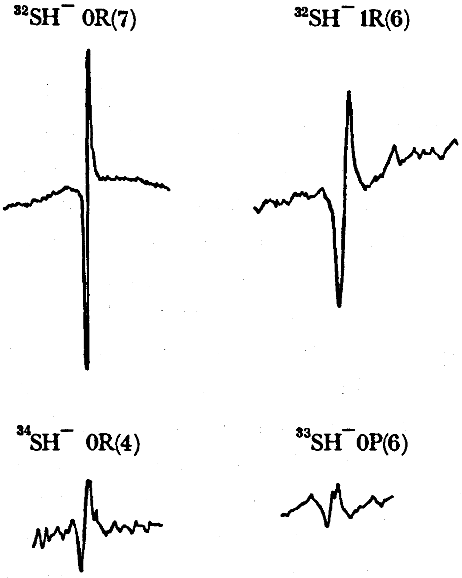

FIGURE 4. Some representative transitions observed for SH^-. The apparent difference in linewidths is caused by the number of channels per line collected by the computer. The number in front of the rotational assignment refers to the lower vibrational state.

walls cooled to 10 °C. Although no enhancement of the anion density was achieved by coating the cell with metal, signal:noise ratios as high as 200 were nevertheless observed for $^{32}SH^-$, allowing both the $^{33}SH^-$ and $^{34}SH^-$ fundamentals as well as the lowest $^{32}SH^-$ hot band to be measured. All of these spectra were fitted simultaneously to a Dunham-type expression with appropriate isotope scaling relations to obtain the equilibrium molecular constants. From the fitted value of B_e, an equilibrium bond distance of 1.343255(14) Å† was obtained for SH^-, compared to the value 1.340379 (5) Å for the neutral SH radical derived from the infrared laser study of Bernath *et al.* (1983). An estimate of the dissociation energy ($D_e = 3.92$ eV) of the anion was obtained by fitting the spectra to a third-order potential function and calculating the coefficients of a Morse function. This agrees well with the value of 3.95 eV obtained from photoelectron spectroscopy.

Amide (NH_2^-)

An extensive spectrum was observed for NH_2^- in the range 2900–3400 cm^{-1}, as shown in figures 5 and 6, with the Berkeley colour-centre laser system. Although its electron binding energy is relatively low (0.76 eV), the NH_2^- ion was readily generated in discharges containing *ca.* 3 Torr of NH_3; apparently the production of amide ions proceeds by dissociative electron attachment to ammonia, because this process has a large cross section (2×10^{-18} cm^{-2}) that peaks at an energy typical of electrons in such plasmas (5.6 eV). A substantial enhancement of the NH_2^- density was also observed when the cell was coated with copper metal. The observed density of NH_2^- was calculated to be approximately 4×10^{11} cm^{-3}. Of the *ca.* 180 vibration–rotation transitions measured, 117 were assigned and fit simultaneously to a Watson *S*-reduced hamiltonian for the ν_1 (symmetric stretch) and ν_3 (asymmetric stretch) bands. Several large perturbations were observed, ostensibly resulting from both Coriolis and Fermi perturbations between the (020) bending state and the two upper stretching states.

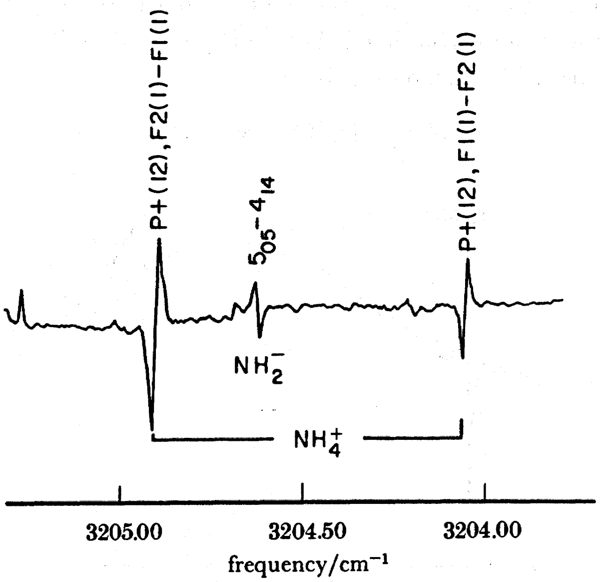

FIGURE 5. Velocity-modulation spectra showing R-branch transition in the ν_1 band of NH_2^- and two lines previously assigned to NH_4^+.

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† 1 Å = 10^{-10} m = 10^{-1} nm.

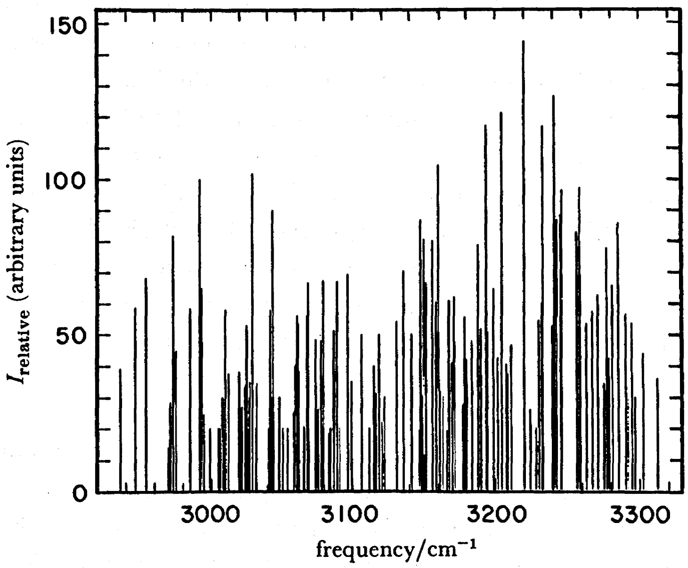


FIGURE 6. Computer plot of all observed lines assigned to NH_2^-.

From the fitted molecular constants, a zero-point geometry was determined; $r_{NH} = 1.0367\,(154)$ Å and $\theta_{HNH} = 102.0\,(3.3)°$. The band origins were: $\nu_1 = 3121.9306\,(61)$ cm^{-1} and $\nu_3 = 3190.291\,(14)$ cm^{-1}. These results are in good agreement with the *ab initio* calculations of Lee & Schaefer (1985) and Botschwina (1986).

Azide (N_3^-)

Figure 7 shows representative spectra of the asymmetric stretching mode of azide anion observed near 2000 cm^{-1} with the diode laser velocity-modulation spectrometer. These spectra were optimized in a discharge through 1.7 Torr NH_3 and 300 mTorr of N_2O. The formation reaction, suggested to us by V. Bierbaum, is

$$NH_2^- + NNO \rightarrow N_3^- + H_2O.$$

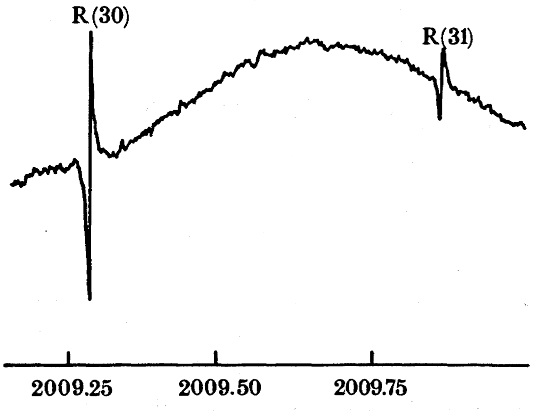


FIGURE 7. Velocity-modulation diode laser spectra of the ν_3 band of N_3^-, showing the 2:1 intensity alternation. The alternation appears larger because of changes in laser power during the scan. The symmetries of the lineshapes identify the transitions as negative-ion absorptions.

The data presented in figure 7 clearly establish the centrosymmetric nature of N_3^- by virtue of the intensity alternation observed between the adjacent rotational lines; spectra measured in crystalline environments were inconsistent in revealing this property.

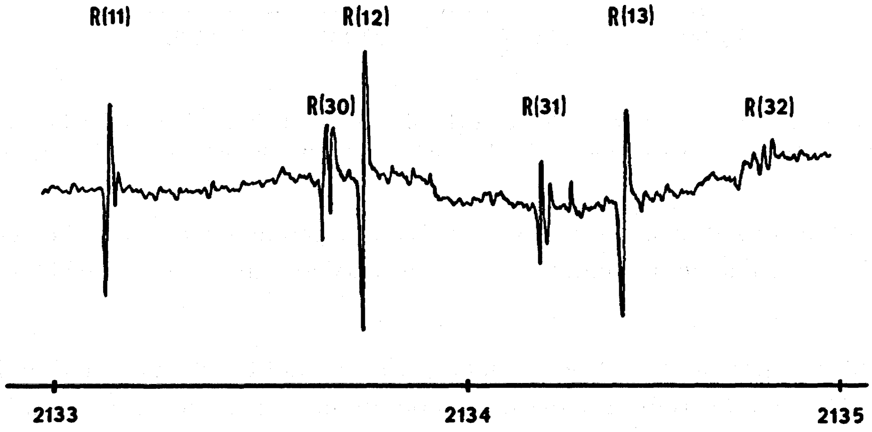
The data, ranging from P(42) to R(62), were fitted to a linear molecule effective hamiltonian including quartic terms. The band origin and rotational constants are: $\nu_3 = 1986.4672\,(19)$ $\mathrm{cm^{-1}}$, $B'' = 0.426\,203\,(57)$ $\mathrm{cm^{-1}}$, and $B' = 0.422\,572\,(55)$ $\mathrm{cm^{-1}}$, yielding 1.188402 (82) Å as the zero-point bond length. These results indicate a significant increase in the bond length relative to results extracted from X-ray crystallographic studies (1.12–1.16 Å).

Cyanate (NCO^-)

Figure 8 shows a portion of the ν_3 band (CN stretch) of NCO^- observed with the diode laser system in the region near 2100 $\mathrm{cm^{-1}}$ in a discharge through NH_3 and CO_2. A variety of hot bands were measured in this work, indicating that the formation reaction suggested by Dr Bierbaum,

$$NH_2^- + CO_2 \rightarrow NCO^- + H_2O,$$

produces high vibrational excitation, particularly in the bending mode.



frequency/cm^{-1}

FIGURE 8. Velocity-modulation spectrum of the most intense R-branch region of the ν_3 band (CN stretch) of NCO^-. The singlets are fundamental lines and the doublets are from the bending hotband.

Over 132 transitions in the CN stretching fundamental and associated bending and stretching hot bands were measured and fitted to a standard linear-molecule hamiltonian, yielding effective parameters for the (00^00), (01^10), (02^00), (10^00), (00^01), (01^01), (02^01), and (10^01) states. Measurement of the rotational constants in all normal modes allowed the determination of the equilibrium rotational constant as 0.385933 (166) $\mathrm{cm^{-1}}$ and the ν_3 fundamental was determined to be 2124.307 $\mathrm{cm^{-1}}$.

Thiocyanate (NCS^-)

The similar formation reaction

$$NH_2^- + CS_2 \rightarrow NCS^- + H_2S$$

was used to produce the NCS^- anion in a NH_3–CS_2 plasma. Figure 9 shows representative spectra observed for the CN stretch with the diode laser system near 2078 $\mathrm{cm^{-1}}$. Again, several

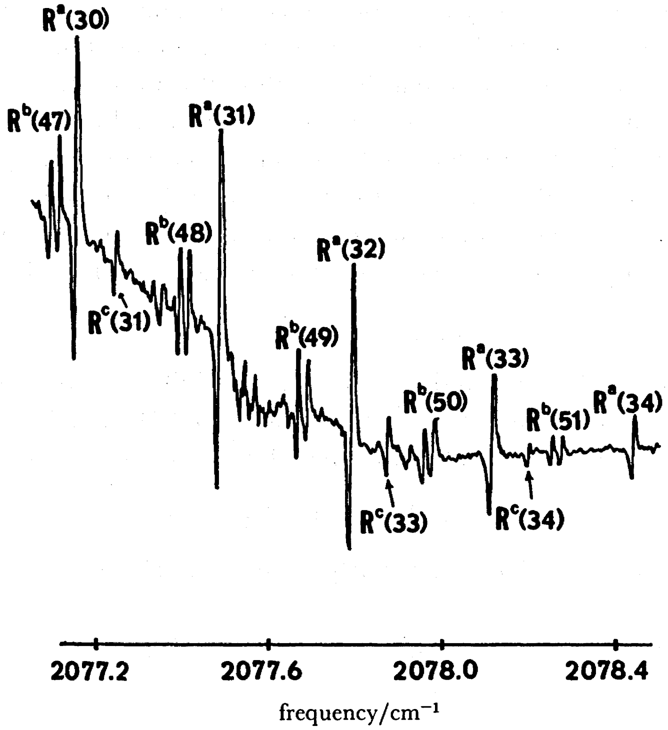


FIGURE 9. Velocity-modulation spectra of the ν_3 band (CN stretch) of NCS$^-$. The superscript label a denotes the fundamental band, b denotes the (01^10–01^11) hot band, and c denotes the (10^00–10^01) hot band.

hot bands were measured, permitting the equilibrium rotational constant to be determined as 0.197438(61) cm^{-1}. The fundamental band origin was determined to be 2065.9302(13) cm^{-1}.

CCH$^-$

Figure 10 shows spectra of the C–C stretching vibration of CCH$^-$ measured with the diode laser system. The anion was formed by the reaction of fluorine atoms, generated from NF$_3$ in the plasma, with acetylene. Optimized discharge mixtures also contained a small amount of O$_2$, which functioned mainly to stabilize the discharge. Twelve transitions [P(12) to R(11)]

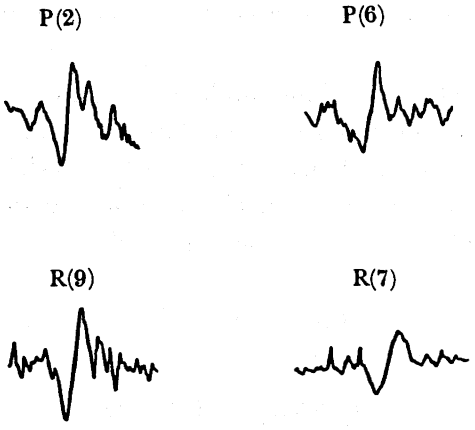


FIGURE 10. Velocity-modulation spectra of the ν_3 band (CC stretch) of CCH$^-$ observed near 1750 cm^{-1}.

were measured and fitted to a linear-molecule hamiltonian. The C–C stretching band origin was found to be 1758.621 (3) cm^{-1} and the ground-state rotational constant was 1.3814 (3) cm^{-1}.

Botschwina (1986) has calculated the dipole moment of CCH^- to be -3.22 D†. Because of the widespread abundance of neutral CCH in interstellar sources, this makes CCH^- an excellent candidate for an interstellar search. Its detection would certainly lead to important knowledge of the roles of negative molecular ions in the chemistry of interstellar molecular clouds.

CONCLUSIONS

Clearly, the development of high-resolution laser spectroscopy of molecular anions has proceeded at an impressive rate over the last two years. At this stage, the seven anions discussed in this article, as well as the extremely interesting FHF^- anion studied by Kawaguchi & Hirota (1986), have been detected by velocity-modulation spectroscopy. In addition, autodetachment methods have now resulted in the observation of high-resolution spectra for several interesting species (NH^-, $C_2H_3O^-$, CH_2CN^-, FeO^-, PtN^-, C_2^-).

One of the important reasons for the success of the velocity-modulation method is the impressive knowledge of anion chemistry generated from the flowing afterglow experiments of Bierbaum *et al.* (1977, 1984) and others. Guided by this work, it appears that a wide variety of negative molecular ions can now be studied in detail by this approach.

An interesting and important result of these laboratory studies of molecular-anion spectra is the generation of a data base for astrophysical searches for negative-ion spectra. Given current estimates of the electron density in cold, dark interstellar clouds, the abundance of several negatively charged molecules such as CCH^-, NCO^-, OH^- and NH_2^- may be sufficient to enable their detection by millimetre astronomy. In fact, searches are currently continuing by this research group for rotational transitions of CCH^- and NCO^- at several observatories, by using data obtained from the experiments described in this paper. It is hoped that successful detection of several of these anions can be accomplished, and that, as a result, we may begin to explore the currently unknown effects of negatively charged molecules in interstellar chemistry.

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† 1 D = 3.33×10^{-30} C m.

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