

Infrared–microwave double resonance spectroscopy of molecular ions: HN_2^+

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Infrared–microwave double resonance spectroscopy has been used to study the simple molecular ion HN_2^+ . This is the first application of this powerful method to a molecular ion. The HN_2^+ ion was produced in a hollow cathode discharge cell, which served two purposes. First, the hollow cathode discharge is capable of producing relatively large concentrations of ions at the low pressures required for saturation. Also, the hollow cathode serves as a waveguide for the propagation of the microwave radiation. A color center laser was used as the infrared source. Its high power was essential in this work for saturation of the infrared transitions. The HN_2^+ ion was chosen as a test case for double resonance because of the availability of detailed spectroscopic information and its ease of production. We have observed the pure rotational transition $J = 1 \leftarrow 0$ in both the ground and ν_1 states using the ν_1 infrared fundamental. The determined molecular constants are $eqQ = -5.88(10)$ MHz and $B = 46\,586.895(18)$ MHz for the ground state, and $eqQ = -5.71(17)$ MHz and $B = 46\,208.986(27)$ MHz for the ν_1 state. The high sensitivity of the double resonance technique has also allowed us to study the direct l -type doubling transitions in the ν_2 and $\nu_1 + \nu_2$ states using the $\nu_1 + \nu_2 \leftarrow \nu_2$ infrared hot band. To the best of our knowledge, this is the first centimeter wave spectrum of a molecular ion. The determined molecular constants are $q = 254.966(11)$ MHz and $q_J = -2.83(17)$ kHz for the ν_2 state, and $q = 258.912(32)$ MHz and $q_J = -3.15(65)$ kHz for the $\nu_1 + \nu_2$ state.

I. INTRODUCTION

Since the astronomical discovery of the emission spectra of molecular ions such as HCO^+ (Ref. 1) and HN_2^+ (Ref. 2) in the early 1970's, there has been an enormous amount of work in the field of molecular ion spectroscopy. The laboratory studies were first performed in the microwave region.³ This was followed by the infrared spectroscopy of molecular ions, which has produced new spectra of many fundamental molecular ions.^{4–6}

The infrared spectroscopy of molecular ions has been greatly facilitated by the development of various modulation methods which are specifically suited for ion detection. These are velocity modulation in an ac glow discharge,⁴ and concentration⁷ and magnetic field modulation⁸ in a hollow cathode discharge.

Recently more sophisticated experimental techniques have been applied to the study of molecular ions. Two examples are vibrational predissociation spectroscopy⁹ and direct infrared absorption spectroscopy in fast ion beams.¹⁰ Also, techniques used first for neutrals have begun to be applied to molecular ions. Stimulated emission pumping¹¹ and two-photon dissociation¹² are two examples.

In this paper we report the first application of infrared–microwave (IR–MW) double resonance spectroscopy to a molecular ion. IR–MW double resonance spectroscopy of neutrals is known to be a powerful method for (a) observing very weak transitions, (b) observing microwave spectra in excited vibrational states, (c) studying collisional processes,

and (d) assigning complicated spectra. Here we apply the method to the simple molecular ion HN_2^+ . This ion was chosen as the test case because of its relative ease of production and the detailed spectroscopic information available.

Since its radio-astronomical observation² and positive identification,^{13,14} HN_2^+ has been extensively studied in the laboratory both through its rotational spectrum and its vibration–rotation spectrum. The rotational spectrum in the ground vibrational state has been observed in the millimeter wave region ($J = 1 \leftarrow 0$),^{15,16} the submillimeter wave region (from $J = 2 \leftarrow 1$ to $5 \leftarrow 4$),¹⁷ and in the far-infrared region ($J = 11 \leftarrow 10$).¹⁸ The vibrational–rotation spectrum of the ν_1 band¹⁹ and its hot band, $\nu_1 + \nu_2 \leftarrow \nu_2$,²⁰ the ν_2 band,²¹ and the ν_3 band⁷ has been observed.

In this work we use the ν_1 band and its hot band, $\nu_1 + \nu_2 \leftarrow \nu_2$, to observe various rotational transitions. The high sensitivity of the double resonance method has enabled us to observe the $J = 1 \leftarrow 0$ rotational transition in the ν_1 state and the direct l -type doubling transitions in the ν_2 and $\nu_1 + \nu_2$ states. The former represents the first observation of the pure rotational transition in an excited state of HN_2^+ . To the best of our knowledge, the latter represents the first observation of molecular ion spectra in the centimeter wave region.

II. EXPERIMENTAL

A block diagram of the IR–MW double resonance experiment is shown in Fig. 1. The spectrometer consists of a krypton ion laser (Spectra Physics 171, operating on the 647 nm line) which pumps a color center laser (Burleigh FCL-20, $\lambda = 2.8\text{--}3.3$ μm , 2–25 mW power using the $\text{RbCl}:\text{Li}$

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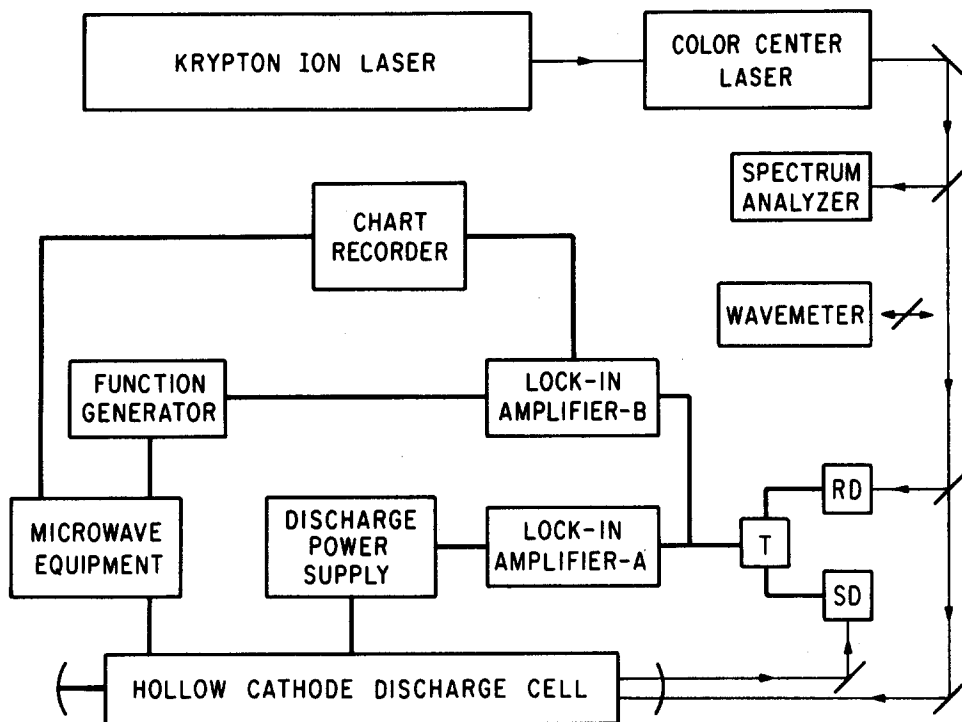


FIG. 1. The IR-MW double resonance spectrometer. The color center laser is continuously tunable from 3000–3600 cm^{-1} with 2–25 mW of power using the $\text{RbCl}:\text{Li}$ crystal. Single mode operation is monitored with a Fabry-Perot spectrum analyzer. The infrared frequency is measured with a wave meter. A portion of the infrared radiation is sent to an InSb reference detector (RD) for noise subtraction. The majority of the infrared radiation is sent to the hollow cathode discharge cell and traverses the cell 12 times before it is detected by an InSb signal detector (SD). Two audio frequency transformers (T) connected 180° out-of-phase subtract the common amplitude noise. The noise subtraction signal is sent to two lock-in amplifiers for phase sensitive detection. Lock-in amplifier A monitors the infrared signal using concentration modulation of the hollow cathode discharge. Lock-in amplifier B monitors the double resonance signal using frequency modulation of the microwave radiation. The double resonance signal is displayed on a chart recorder. The microwave equipment is shown in Fig. 3.

crystal). The infrared laser is continuously tunable using an output grating, a temperature-stabilized intracavity étalon, and a cavity folding mirror. A small portion of the infrared radiation is sent (using a CaF_2 window) to a Fabry-Perot spectrum analyzer for monitoring single mode operation. Another portion of the radiation is sent (using a second CaF_2 window) to a liquid- N_2 -cooled InSb reference detector for noise subtraction. The majority of the radiation is focused at the entrance of a set of White cell mirrors separated by 2.4 m, and traverses the discharge cell 12 times. It is then detected by a second liquid- N_2 -cooled InSb signal detector, matched to the reference detector. The output voltages from

the reference and signal detectors are balanced and sent to a pair of audio frequency transformers connected 180° out-of-phase, in order to subtract the common amplitude noise from the color center laser. The high power of the color center laser is essential in this work for saturating the infrared transitions, in order to observe the pure rotational transition in the ν_1 state and to study the l -type doubling in the ν_2 and $\nu_1 + \nu_2$ states.

The HN_2^+ ion is produced in a hollow cathode discharge cell, as shown in Fig. 2. The cell is similar to one designed by Van den Heuvel and Dymanus,¹⁸ except that the outer glass tube surrounding the cathode is absent in our

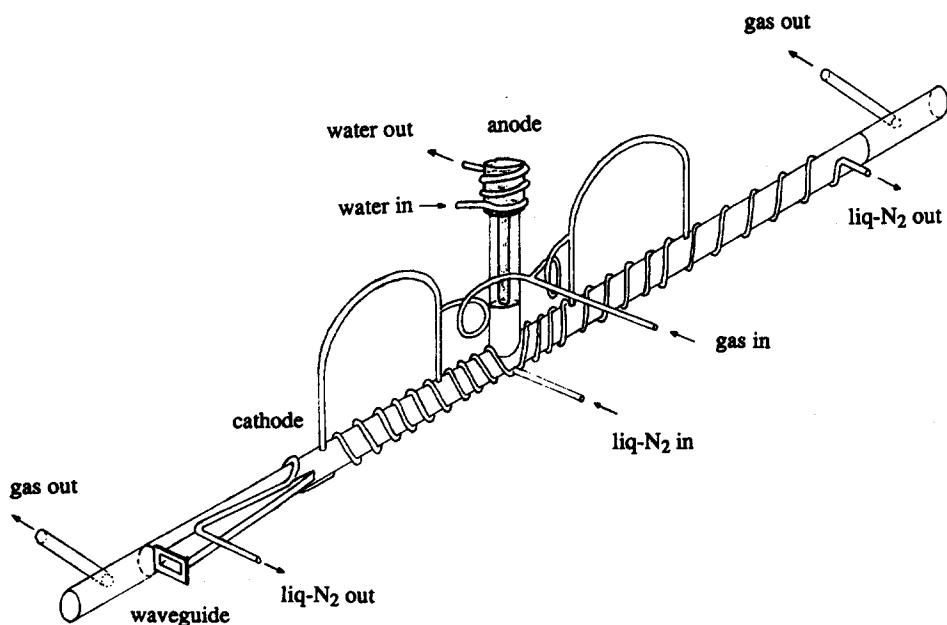


FIG. 2. The hollow cathode discharge cell used to produce HN_2^+ at the low pressures needed for saturation. A gas mixture of nitrogen and hydrogen ($[\text{N}_2]/[\text{H}_2]$ varies from 1 to 3) of total pressure 20–100 mTorr is used. The circular copper cathode is 1.2 m long with a 7/8 in. i.d. The cathode is liquid- N_2 cooled and the anode is water cooled. An ac voltage (500–1000 V, 0.5–1 A, at 20 kHz) is applied to the anode while the cathode is held at ground. Because of the electrode arrangement, the hollow cathode discharge works as a rectifier such that the discharge turns on only when the anode is positive relative to the cathode. The concentration of the molecular ions produced in the discharge is therefore modulated with almost 100% efficiency.

cathode. The circular copper cathode is 1.2 m long with a 7/8 in. i.d. The cathode is cooled by slowly flowing liquid N_2 through helical copper tubing, which was soldered around the cathode. The discharge is struck between the cathode (held at ground) and an anode positioned at the end of a glass-to-metal connection, at the middle of the cathode. The power for the discharge is provided by a Plasmaloc RS-8 power supply (500–1000 V, 0.5–1 A, at 20 kHz). The anode is a water-cooled stainless steel tube (1/2 in. o.d.) which reaches down to the cathode (2–3 in. from the center of the cathode). After the discharge is lit at higher pressures ($P = 50\text{--}200$ mTorr), the pressure can be reduced ($P = 20$ mTorr) with stable operation retained. A gas mixture of nitrogen and hydrogen ($[\text{N}_2]/[\text{H}_2]$ varies from 1 to 3) of total pressure 20–100 mTorr is used. Because of the electrode arrangement, the breakdown voltage is much higher when the anode is negative relative to the cathode. Therefore, when applying an ac voltage to the anode, the hollow cathode discharge cell works as a rectifier such that the discharge turns on only when the anode is positive. Thus, the concentration of molecular ions produced in the discharge is modulated with almost 100% efficiency.⁵ The hollow cathode discharge cell is essential in this work for two reasons. First, the hollow cathode discharge is capable of producing relatively large concentrations of ions ($10^{10}\text{--}10^{11}$ cm^{-3}) at the low pressures needed for saturation. Second, the circular cathode serves as a waveguide for the propagation of the microwave radiation.

The microwave equipment used for observing the pure rotational transitions ($J = 1 \leftarrow 0$) is shown in Fig. 3(a). The microwave radiation is generated by a water-cooled millimeter wave klystron (Varian, 87.1–93.3 GHz, 200–450 mW) which is controlled by a Micro-Now 756 power supply. The millimeter wave radiation is frequency modulated at 40 or 100 kHz with a modulation depth of 200 kHz to 10 MHz. Ninety percent of the radiation is coupled to the hollow cathode through a microwave transition, which is connected to an X-band waveguide which is soldered to the cell at an angle of 20°. The remaining radiation is mixed in a harmonic mixer (Micro-Now HM-W) with a harmonic of the centimeter wave radiation (~ 50 mW) from an automatic phase-locked oscillator (CTI A-142B, 11.32–11.87 GHz), which is externally referenced to a radio frequency synthesizer (PTS 160, 0.1–160 MHz). The beat of the mixing is detected by a phase-locked-loop synthesized receiver (Sony ICF 2010) and is used for frequency measurement. The beat is also monitored using a spectrum analyzer (HP 8554B). The power is measured with a W-band crystal detector (Dorado CD-10) in place of the harmonic mixer.

The microwave equipment used for studying the l -type doubling transitions is shown in Fig. 3(b). The microwave radiation is provided by a synthesized centimeter wave signal generator (HP 8672A, 2–18 GHz), which is power amplified (Hughes 1277H TWTA, 12–18 GHz, 20 W). The power is measured with a thermistor detector (HP 486A). The radiation is frequency modulated at 100 kHz with a modulation depth of 1.5 MHz.

The experiments are performed as follows. The color center laser frequency is adjusted to the peak of the Doppler-

broadened infrared transition by observing the infrared power using concentration modulation (at 20 kHz) and phase sensitive detection (EG&G 5101). The infrared power is also monitored at the modulation frequency of the microwave radiation using phase sensitive detection (Stanford SR510). The frequency of the microwave radiation is then swept. The double resonance signal is observed as a change in infrared absorption at the modulation frequency of the microwave radiation when the microwave frequency is resonant with a molecular transition. For all experiments the planes of polarization of the infrared and microwave radiations are perpendicular to each other.

III. RESULTS AND DISCUSSION

A. Pure rotational transitions

The energy levels for observing the pure rotational transitions in the ground and ν_1 vibrational states are shown in Fig. 4. The $R(1)$ or $P(1)$ infrared transition is used. An example of observed double resonance signals is shown in Fig. 5. The $J = 1$ rotational levels exhibit splitting due to nuclear quadrupole hyperfine structure (from the outer nitrogen). The frequency of the observed rotational transitions can be expressed by

$$\nu = \nu_0 - eqQf(I,J,F) \quad (1)$$

with

$$\nu_0 = 2B - 4D, \quad (2)$$

where B is the rotational constant, D is the centrifugal distortion correction to B , eqQ is the nuclear quadrupole coupling constant, $f(I,J,F)$ is Casimir's function,²² and $F = I + J$. With $I = 1$ for nitrogen, F takes on the values 0, 1, and 2. The frequencies of the observed transitions are listed in Table I, together with ν_0 and eqQ determined by Eq. (1) using a linear least-squares fit. From Eq. (2) the rotational constants are determined using the D value given by Sastry *et al.*,¹⁷ and assuming D in the ground and ν_1 state is the same (see Table II). From $B_0 - B_1 = \alpha_1$, α_1 is also determined as listed in Table II.

As discussed above, HN_2^+ is produced in a hollow cathode discharge cell. The discharge is operated at low pressures ($P \approx 20$ mTorr with $[\text{N}_2]/[\text{H}_2] \sim 1$) in order to achieve infrared saturation, which makes possible the observation of the rotational transition in the ν_1 vibrational state. It is also necessary to operate at low pressures in order to reduce pressure broadening, which allows the hyperfine structure to be resolved. However, at higher pressures ($P \approx 90$ mTorr with $[\text{N}_2]/[\text{H}_2] \sim 3$) a large double resonance signal ($S/N \sim 500$) is observed at the expense of resolution in the ground state as shown in Fig. 5. The ion density at this pressure can be calculated from Beer's law and the infrared cross section formula. We use our observed rotational and vibrational temperatures of 200 and 250 K, respectively, our observed infrared fractional absorptions, and an assumed translational temperature of 200 K. The HN_2^+ number density is then calculated to be 3×10^{10} cm^{-3} using the experimental band intensity.²³

Our experiments rely on infrared and microwave satu-

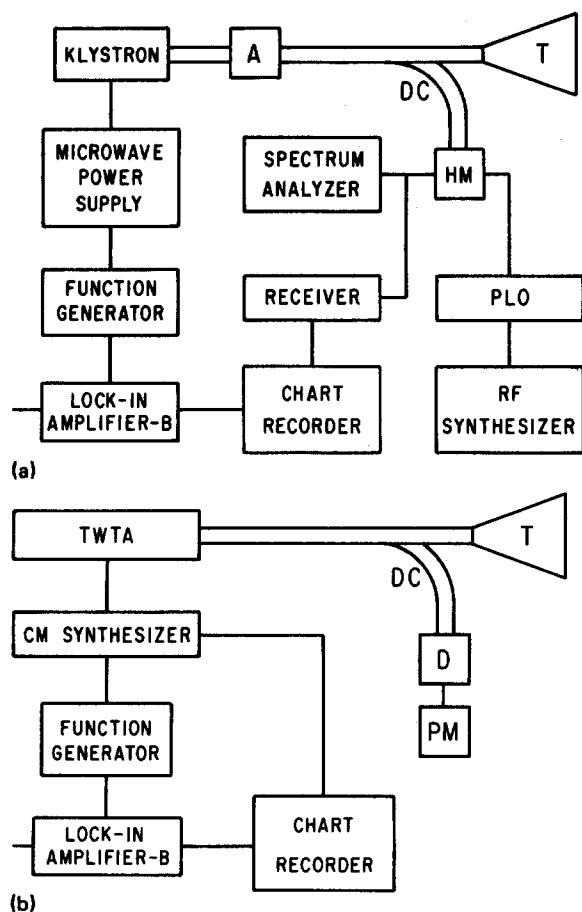


FIG. 3. (a) The microwave equipment for observing pure rotational transitions, $J = 1 \leftarrow 0$. The microwave radiation, generated by a millimeter wave klystron which is controlled by a microwave power supply, is sent through an attenuator (A) and a transition (T) to the hollow cathode discharge cell. A function generator is used to frequency modulate the microwave radiation. The microwave frequency is swept using a stepping motor attached to the reflector voltage control of the power supply. A portion of the microwave radiation is sent to a harmonic mixer (HM) using a directional coupler (DC) and mixed with a harmonic from an automatic phase-locked oscillator (PLO) which is externally referenced to a radio frequency synthesizer. The beat of the mixing is detected by a synthesized receiver which produces a marker on the chart recorder for frequency measurement of the double resonance signals. (b) The microwave equipment for observing the l -type doubling transition. The microwave radiation, generated by a synthesized centimeter wave signal generator, is power amplified by a traveling wave tube amplifier (TWTA) before being sent through a transition (T) to the hollow cathode discharge cell. A function generator is used to frequency modulate the microwave radiation. The microwave frequency is swept using a stepping motor attached to the frequency control of the centimeter wave generator. A portion of the radiation is sent to a thermistor detector (D) using a directional coupler (DC) for measuring the power (PM = power meter). The microwave frequency is continuously monitored with markers periodically produced on the chart recorder for frequency measurement of the double resonance signals.

ration. Saturation occurs when the Rabi frequency is comparable to or larger than the collisional frequency. The Rabi frequency ($\mu_{ij}E/h$) is the frequency at which the radiation transfers molecules from state i to state j , where μ_{ij} is the transition dipole moment and E is the radiation's electric field. The collisional frequency can be equated to the pressure-broadened linewidth. Using a discharge with a total

pressure of 20 mTorr, the linewidth is estimated to be 0.4 MHz, HWHM.²⁴ With 10 mW of infrared power, a beam diameter of 2 mm, and $\mu_{ij} = 0.1$ D [for $R(1)$], the infrared Rabi frequency is ~ 0.9 MHz. Using 50 mW of microwave power, a hollow cathode diameter of 2.4 cm, and $\mu_{ij} = 1.9$ D (for $J = 1 \leftarrow 0$), the millimeter wave Rabi frequency is ~ 3.1 MHz. Therefore, both radiations are intense enough to saturate. This is confirmed by noting that the double resonance signal in the ν_1 state is as strong as that in the ground state (see Fig. 4). The large millimeter wave Rabi frequency is an overestimate because it assumes 100% propagation efficiency in the hollow cathode discharge cell. Because of impedance mismatches from the klystron to the cathode and because of poor mode quality in the cathode, the millimeter wave propagation efficiency is less than 100% and could be as low as 10%.

B. l -type doubling transitions

Rotational levels of a linear polyatomic molecule in a degenerate excited vibrational state with vibrational angular momentum $l = 1$ are split by l -type doubling. The ν_2 bending vibration in HN_2^+ is doubly degenerate and exhibits l -type doubling when $v = 1$, $l = 1$. Using the infrared hot band $\nu_1 + \nu_2 \leftarrow \nu_2$, we were able to study the l -type doubling in both vibrational states. An example energy level diagram is shown in Fig. 6. The splitting is given by

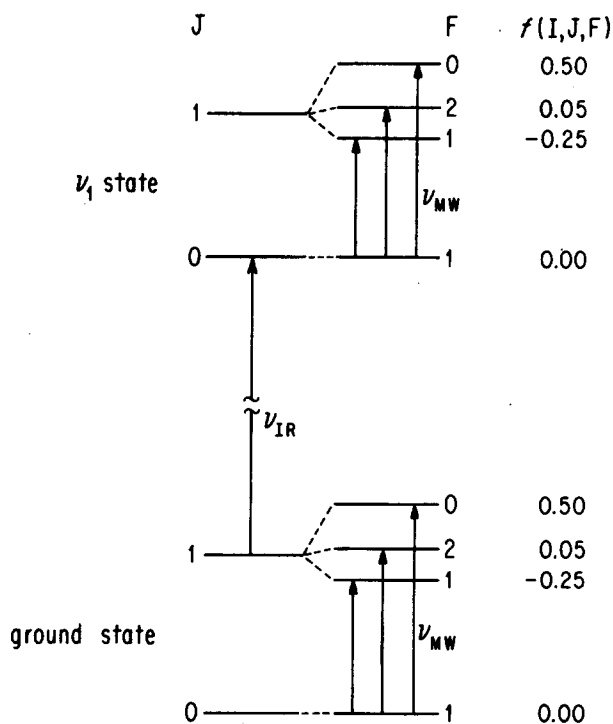


FIG. 4. The energy level diagram for observing the pure rotational transitions $J = 1 \leftarrow 0$ in the ground and ν_1 vibrational states using the ν_1 fundamental. The rotational levels exhibit splitting due to nuclear quadrupole hyperfine structure. Only the splitting from the outer nitrogen could be resolved. $F = I + J$, where $I = 1$ for nitrogen, and $f(I, J, F)$ is Casimir's function.

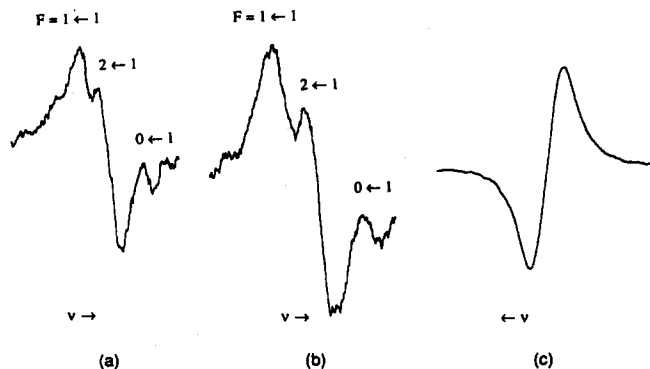


FIG. 5. The $J = 1-0$ rotational transition of HN_2^+ at 93 GHz observed with IR-MW double resonance spectroscopy by monitoring the $R(1)$ or $P(1)$ infrared transition of the ν_1 fundamental while sweeping the microwave radiation. The nitrogen nuclear quadrupole hyperfine structure (due to the outer nitrogen) is resolved in (a) the ν_1 vibrational state and (b) the ground vibrational state. The experimental conditions are total pressure = 25 mTorr, IR power = 10 mW, MW power = 50 mW, FM modulation of the microwave at 40 kHz with modulation depth of 0.5 MHz, and a 10 s time constant. The signal-to-noise ratio could be increased at the expense of resolution in the ground state, (c) by increasing the total pressure to 90 mTorr, the MW power to 400 mW, and the FM modulation depth to 10 MHz. [The phase reversal in (c) occurs because the microwave frequency was swept down, whereas in (a) and (b) it was swept up.]

$$\Delta\nu = [q + q_J J(J+1)] J(J+1), \quad (3)$$

where q is the l -type doubling constant and q_J is the centrifugal distortion correction to q .

We observed the splitting in the ν_2 state for $J = 6, 7$, and 8, and in the $\nu_1 + \nu_2$ state for $J = 6$ and 7. The transitions which could be observed were limited by the frequency range of the microwave equipment. An example signal is shown in Fig. 7. The measured frequencies and determined constants

TABLE I. Observed pure rotational transitions and determined hyperfine structure constants (in MHz).

| | This work ^a | Gudeman ^b | Cazzoli <i>et al.</i> ^c |
|---------------------------|------------------------|----------------------|------------------------------------|
| Ground state | | | |
| $\nu(F=0-1)$ | 93 176.36(10) | 93 176.271(70) | |
| $\nu(F=2-1)$ | 93 173.78(10) | 93 173.719(10) | |
| $\nu(F=1-1)$ | 93 171.94(10) | 93 171.969(20) | |
| ν_0 | 93 173.439(35) | 93 173.419(50) | 93 173.435(3) |
| $eqQ(\text{outer})$ | - 5.88(10) | - 5.75 | - 5.71(3) |
| $eqQ(\text{inner})$ | ... | ... | - 1.44(4) |
| C_N | ... | 0.012 | 0.012(4) |
| ν_1 vibrational state | | | |
| $\nu(F=0-1)$ | 92 420.45(10) | | |
| $\nu(F=2-1)$ | 92 417.98(10) | | |
| $\nu(F=1-1)$ | 92 416.15(10) | | |
| ν_0 | 92 417.622(54) | | |
| $eqQ(\text{outer})$ | - 5.71(17) | | |
| $eqQ(\text{inner})$ | ... | | |
| C_N | ... | | |

^a Frequencies listed are the average of two to three measurements with one σ reported.

^b From Ref. 24.

^c From Ref. 16.

TABLE II. Derived molecular constants (in MHz).

| | This work ^a | Owrutsky <i>et al.</i> ^b | Sastry <i>et al.</i> ^c |
|---------------------------|------------------------|-------------------------------------|-----------------------------------|
| Ground state | | | |
| B | 46 586.895(18) | 46 586(1) | 46 586.863(15) |
| $D(\times 10^3)$ | 87.50 ^d | 87.72(78) | 87.50(53) |
| ν_1 vibrational state | | | |
| B | 46 208.986(27) | 46 208(1) | ... |
| $D(\times 10^3)$ | 87.50 ^d | 86.85(69) | ... |
| α_1 | 377.909(45) | 378(1) | ... |

^a Reported errors are one σ .

^b From analysis of infrared spectra [Ref. 20, Table I (case 2)].

^c From analysis of millimeter and submillimeter spectra (Ref. 17).

^d Fixed to the ground state value given by Sastry *et al.* (Ref. 17).

are listed in Table III. Before our study the only determination of q came from the infrared spectroscopic work.

For the l -type doubling study a total pressure of 60 mTorr is used ($[\text{N}_2]/[\text{H}_2] \sim 2$). This gives a pressure-broadened linewidth of ~ 1.2 MHz. Using 23 mW of infrared power, and $\mu_{ij} = 0.1$ D [for $R(6)$], the infrared Rabi frequency is ~ 1.3 MHz. Using 6 W of microwave power, and $\mu_{ij} = 0.3$ D (for $J = 6$), the microwave Rabi frequency is ~ 5.2 MHz. Again, both radiations are intense enough to saturate. Also, the microwave propagation efficiency is again less than 100%.

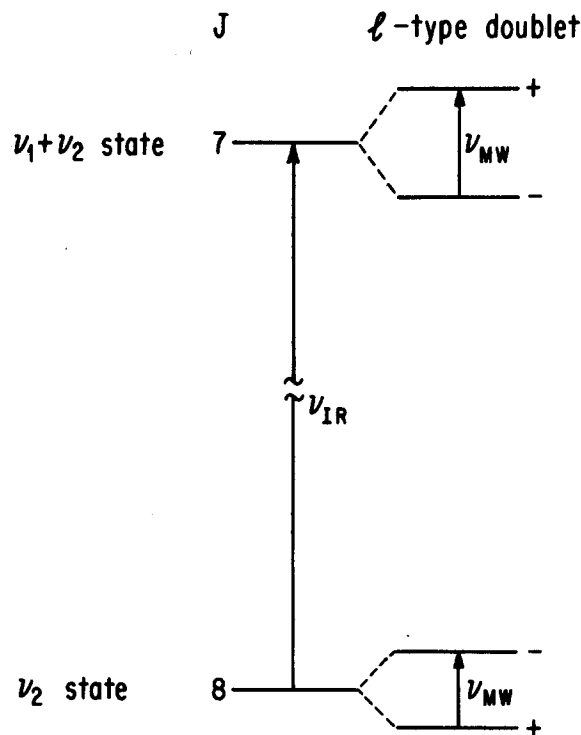


FIG. 6. The energy level diagram for observing the l -type doubling transitions in the ν_2 and $\nu_1 + \nu_2$ vibrational states using the hot band $\nu_1 + \nu_2 \leftarrow \nu_2$. Transitions were observed for $J = 6, 7$, and 8 in the ν_2 state, and for $J = 6$ and 7 in the $\nu_1 + \nu_2$ state. The designations + and - refer to the parity of the level.

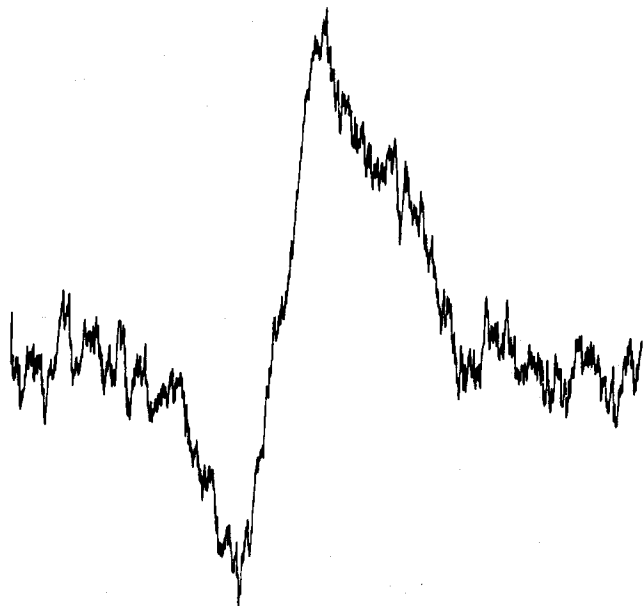


FIG. 7. An *l*-type doubling transition ($J = 8$) in the ν_2 state of HN_2^+ at 18 GHz observed with IR–MW double resonance spectroscopy by monitoring $P(8)$ of the infrared hot band $\nu_1 + \nu_2 \leftarrow \nu_2$, while sweeping the microwave radiation. The experimental conditions are total pressure = 44 mTorr, IR power = 23 mW, MW power = 6 W, FM modulation of the microwave radiation at 100 kHz with modulation depth of 1.5 MHz, and a 10 s time constant.

IV. CONCLUSIONS

As pointed out in the Introduction, IR–MW double resonance spectroscopy is a powerful tool for studying neutrals. In this paper we have shown that it is now a powerful tool for studying molecular ions. It has several advantages over conventional microwave spectroscopy. First, observations of very weak transitions are possible. Our study of the *l*-type doubling in the ν_2 and $\nu_1 + \nu_2$ vibrational states would have been extremely difficult to do with conventional microwave spectroscopy. Second, observation of microwave spectra in excited vibrational states is possible. As pointed out earlier, pure rotational transitions of HN_2^+ had never been observed in any excited vibrational state before this work. Third, studies of collisional processes are possible. We have begun to study the collisional processes in HN_2^+ .²⁵ While similar in-

TABLE III. Observed *l*-type doubling frequencies^a and constants (in MHz).

| | ν_2 vibrational state | $\nu_1 + \nu_2$ vibrational state |
|--------------|----------------------------|-----------------------------------|
| $\nu(J = 6)$ | 10 703.47(45) | 10 868.74(18) |
| $\nu(J = 7)$ | 14 269.38(34) | 14 489.18(27) |
| $\nu(J = 8)$ | 18 342.83(34) | ... |
| q | 254.966(11) ^{b,c} | 258.912(32) ^c |
| q_J | $-2.83(17) \times 10^{-3}$ | $-3.15(65) \times 10^{-3}$ |

^a Frequencies are the average of two to three measurements with one σ reported.

^b Infrared ν_2 band analysis gives $q = 254.44(9)$ MHz. (From Ref. 21.)

^c Infrared $\nu_1 + \nu_2 \leftarrow \nu_2$ hot band analysis gives $q(\nu_2) = 251.74(69)$ MHz, $q(\nu_1 + \nu_2) = 255.51(66)$ MHz. (From Ref. 20, Table II.)

formation could be obtained from microwave–microwave double resonance spectroscopy, the wide tunability of the color center laser makes the IR–MW double resonance method more widely applicable. Fourth, complicated spectra can be unravelled. This point suggests that IR–MW double resonance spectroscopy of molecular ions should complement infrared spectroscopy of molecular ions. We hope to apply this technique to clarify the complicated spectrum of C_2H_3^+ .²⁶

To increase the sensitivity of the spectrometer, the following improvements are being considered. The microwave saturation can be increased by reducing the cathode diameter and increasing the microwave propagation efficiency. The infrared saturation can be increased by building an external optical cavity around the hollow cathode discharge cell. Also, if we stabilize the klystron (the present experiments were performed using a free-running klystron), signal averaging of the double resonance signal will increase the sensitivity.

We plan to apply IR–MW double resonance spectroscopy to other ions, including H_2D^+ , HCNH^+ , NH_4^+ , and CH_3CNH^+ .

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