Observation of direct and collision-induced double resonance of a molecular ion

C. J. Pursell, D. P. Weliky,[a] W. C. Ho, K. Takagi,[b] and T. Oka
Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

(Received 31 August 1989; accepted 9 October 1989)

Double resonance is a powerful technique for increasing sensitivity,[1] for assigning complex spectra,[2] for observing very weakly allowed transitions,[3] and for studying rotational energy transfer.[4] We report here our recent application of this technique to the HN_2^+ molecular ion. We have observed not only the direct three-level double resonance signals both in the ground and the excited states, but also collision-induced four-level double resonance signals indicating the existence of some selection rules even for the Langevin potential dominated ion–neutral interaction.

We used a hollow cathode (1″ diameter and 1 m long) as the double resonance cell. The hollow cathode discharge was chosen for our ion double resonance because (a) it provides abundant ($\sim 1 \times 10^{11}$ cm^{-3}) ions[5] at relatively low pressures (20–200 mTorr) needed for infrared and microwave saturation, and (b) the metal wall of the cathode serves as a waveguide for the microwave radiation. A color center laser with 2–20 mWatts of power provided the infrared *signal* radiation, and a millimeter wave klystron with ~ 400 mWatts of power provided the microwave *pump* radiation. The frequency of the microwave radiation was swept and the double resonance signal was detected through the variation of infrared power.

The observed $J = 1 \leftarrow 0$ rotational transitions in the ground and the ν_1 state are shown in Fig. 1. Observation of the signal in the ν_1 state indicates that the infrared radiation was at least partially saturating the infrared transition used in the experiment. In order to resolve the nitrogen nuclear quadrupole hyperfine structure, the pressure and microwave power were reduced to avoid broadening. When they were increased at the expense of resolution, a signal to noise ratio of ~ 400 was observed. With this arrangement, we could also observe collision-induced four-level double resonance signals which are typically 10–100 times weaker than the direct double resonance signal.

The energy level system used in the experiment is shown in Fig. 2. In the three-level experiment, the variation of the molecular population in the $J = 1$ level due to the micro-

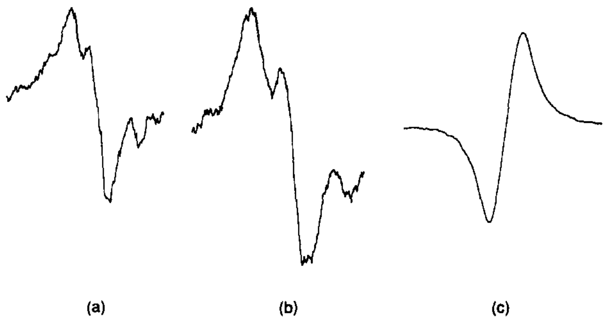

FIG. 1. The $J = 1 \leftarrow 0$ rotational transition of HN_2^+ at 93 GHz observed with microwave-infrared (MW-IR) double resonance spectroscopy by monitoring the $R(1)$ or $P(1)$ infrared transition (at 3240.094 and 3230.844 cm^{-1}, from Ref. 11) while sweeping the microwave radiation. The nitrogen nuclear quadrupole hyperfine structure is resolved in (a) the ν_1 vibrational state [at 92 420.45(10), 92 417.98(10), and 92 416.15(10) MHz] and (b) the ground vibrational state [at 93 176.36(10), 93 173.78(10), and 93 171.94(10) MHz; cf. 93 176.271 (70), 93 173.719(10), and 93 171.969(20) MHz, from Ref. 9] with total pressure = 25 mTorr, IR power = 10 mWatts, MW power = 50 mWatts, FM modulation of the MW at 40 KHZ with modulation depth of 0.5 MHz and 10 second 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 mWatts 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.]

wave radiation (ν_p) affects the infrared signal (left in Fig. 2) directly, while in the four-level experiment the variations in the $J = 1$ and $J = 0$ levels are transferred to the $J = 2$ level through collision. The collision-induced signals were observed to have the same phase as the direct signal indicating that the collision-induced populational transfer between the $J = 2$ and $J = 1$ levels (α in Fig. 2) has a larger rate than that between $J = 2$ and $J = 0$ (γ in Fig. 2). When N_2 was the dominant collision partner, we observed collision-induced signals as strong as 10% of the direct signal indicating the strong preference of the dipole-type α transition to the quadrupole-type γ transition. Existence of such selection rules has been noted for neutral polar molecules,[6,7] but the observation of similar rules with such clarity for ion-neutral collisions is remarkable.

The ion–neutral collision is qualitatively different from the neutral collision because of the presence of the $1/r^4$ Langevin potential.[8] This potential is independent of the ion's angular coordinates once the electric effect due to the difference between the center of charge and the center of mass is incorporated into the effective dipole moment. Therefore the Langevin potential itself does not cause rotational transitions of the molecular ion. Its effect is to exert an intermolecular force which is *always* attractive and thus to reduce the ion–molecule distance. This in effect makes the angular dependent forces stronger. This argument is supported by Gudeman and Woods'[9] report that the pressure broadening of HCO^+ is larger than that of HCN by a factor of 3–4.

The effect of $J = 1 \leftarrow 0$ microwave pumping has been observed not only in the neighboring $J = 2$ level, but also in the $J = 3$ and 4 levels. The signals ranged between 0.5%–5% of the direct signal with comparable magnitude for both N_2-dominated and He-dominated discharges. Their phase is always the same as the direct signal indicating that the $J = J_f \leftarrow 1$ transition has a larger rate than the $J = J_f \leftarrow 0$ transition, where $J_f = 2$, 3, or 4. Such preference was predicted by Green[10] for HN_2^+–He collisions, but the present observation seems to give higher preference.

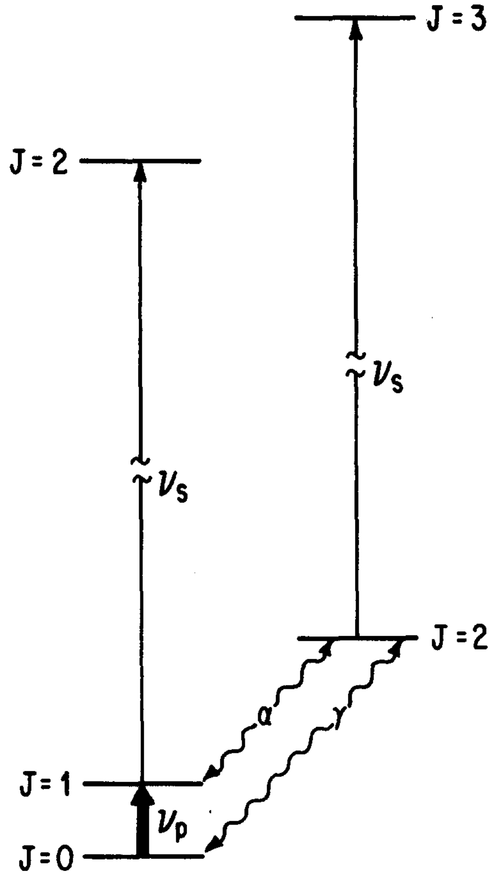

FIG. 2. In the three-level double resonance (left side only) the molecular population variation produced in the $J = 1$ level by the microwave radiation (ν_p) directly affects the infrared signal (ν_s). In the four-level double resonance the variations in the $J = 1$ and $J = 0$ levels are transferred to the $J = 2$ level through collision. The four-level double resonance signal is observed when the molecular transfer obeys selection rules; i.e., when either the α transition (dipole-type) or the γ transition (quadrupole-type) is strongly preferred over the other. The phase of the observed signal indicates that the α transition rate is larger than the γ transition rate.

The major results of this paper are: (1) The double resonance method is now applicable to molecular ions and (2) ion–molecule collisions have selection rules. More extensive results, in particular the comparison with HCN and observation of the l-doubling spectrum, will be published in the near future. We believe this method is applicable to other ions, especially the protonated ions which exist abundantly in hollow cathode discharges.

This work has been supported by NSF grant PHY 87-07025. We also acknowledge the partial support of the Petroleum Research Foundation administered by the American Chemical Society. K. Takagi acknowledges an overseas scholarship from the Ministry of Education, Science, and Culture of Japan.

[a] NSF Predoctoral Fellow.

[b] Permanent address: Department of Physics, Toyama University,

Gofuku, Toyama 930, Japan.

[1] H. Jones, *Modern Techniques of Microwave Spectroscopy*, edited by G. W. Chantry (Academic, New York, 1979), pp. 123–216.

[2] See for example, S. L. Coy, K. K. Lehmann, and F. C. DeLucia, J. Chem. Phys. **85**, 4297 (1986).

[3] T. Oka, *Molecular Spectroscopy: Modern Research*, edited by K. Narahari Rao (Academic, New York, 1976), Vol. II, pp. 229–253.

[4] T. Oka, *Advan. At. Mol. Phys. 9* (Academic, New York, 1973), pp. 127–206.

[5] See for example, T. Amano and K. Tanaka, J. Chem. Phys. **83**, 3721 (1985).

[6] R. M. Lees and T. Oka, J. Chem. Phys. **51**, 3027 (1969).

[7] P. W. Daly and T. Oka, J. Chem. Phys. **53**, 3272 (1970).

[8] P. Langevin, Ann. Chim. Phys. **5**, 245 (1905).

[9] C. Gudeman, Thesis, University of Wisconsin (1982).

[10] S. Green, Astrophys. J. **201**, 366 (1975).

[11] J. C. Owrutsky, C. S. Gudeman, C. C. Martner, L. M. Tack, N. H. Rosenbaum, and R. J. Saykally, J. Chem. Phys. **84**, 605 (1986).