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important in intersteller chemistry occurring on grain surfaces.

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Difference frequency laser spectroscopy of the ν_1 band of HOCO+

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In 1981, Thaddeus, Guelin, and Linke[1] attributed three harmonically related unidentified millimeter-wave lines observed in SgrB2 to either HOCO+ or HOCN. Later DeFrees et al.[2] suggested that HOCO+ was the more likely candidate, based on a comparison of the ab initio calculated rotational constants with the "observed". Several attempts[3] have been made in various laboratories to detect the microwave lines of HOCO+ for conclusive confirmation of this tentative assignment. Quite recently, Bogey, Demuynck, and Destombes[4] finally succeeded in detecting submillimeter-wave absorption lines of HOCO+ around 370 GHz. In this Communication, we report the first observation of the infrared spectrum of this ion, thus providing an independent confirmation of the identification of interstellar HOCO+.

The experimental technique used in the present work is similar to that in our previous experiments.[5] One modification made here was that a hollow cathode discharge cell replaced the previous conventional glow discharge cell. The hollow cathode cell is of similar design to that employed by Foster et al.[6] and Foster and McKellar.[7] Some preliminary tests[8] done by monitoring the lines of H_3^+, H_2D^+, and HCO+ indicated that the signal intensity was enhanced at least by an order of magnitude compared with that obtained using our previous glow discharge cell.

The HOCO+ ions were generated in a modulated discharge through a flowing gas mixture of CO_2 (20 mTorr) and H_2 (250 mTorr). The discharge was cooled by allowing methanol at about $-50°$ C to flow through copper tubing wound around the cathode. The discharge modulation frequency was 5 kHz, and the optimum peak current was about 800 mA. The application of an axial magnetic field of 150 G to the cathode glow resulted in almost total loss of the ion signals[8] similar to the effect reported by Saito et al.[9] This phenomenon has been observed also on the known ions such as H_3^+, H_2D^+, and HCO+.[8]

The HOCO+ is a bent molecule with an almost linear O–C–O structure.[10–12] Both the a-type and b-type transitions were observed. At first it was noticed that the spectral pattern repeated itself with approximately 0.7 cm^{-1} interval, and the lines were readily assigned to the a-type P- and R-branch transitions. Figure 1 is an example of the signals which are assigned to the $^PQ_1(J)$ transitions with partial overlaps by P- or R-branch lines. At the present stage, nearly 300 lines have been observed. The transition wave numbers were measured with N_2O lines as reference,[13] and the accuracy of our measurement is estimated to be better than 0.001 cm^{-1}. The difference between the frequencies for $^qR_0$ (15) and $^qP_0$ (17) transitions was found to be 705 454 MHz which agreed within our measurement accuracy with the sum of the transition frequencies of the $J = 17–16$, $K = 0$ and the $J = 16–15$, $K = 0$ lines observed by Bogey et al.[4] A similar check was done on the $K = 2$ lines.

A preliminary least-squares fit was made with a standard asymmetric-top Hamiltonian in the A-reduced representation,[14] including 176 lines of the a-type P- and R-branch lines of $K = 0$, 1, and 2, and the b-type Q-branch lines of $K = 0–1$ and $K = 1–0$. The rotational constants, B_0

HOCO+ $^PQ_1(J)$
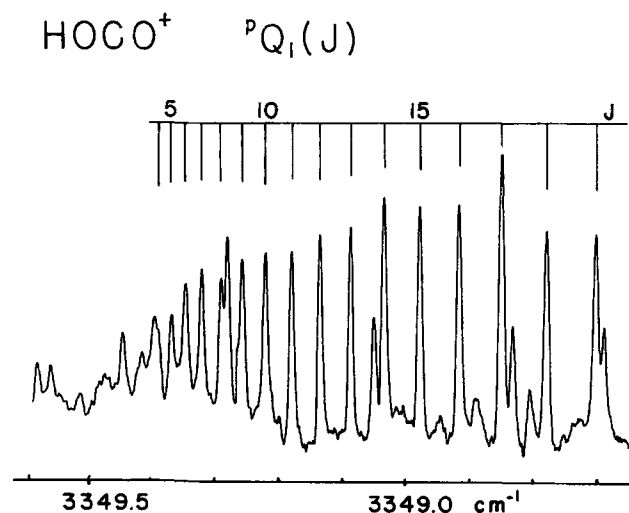

FIG. 1. The $^PQ_1(J)$ transitions of the ν_1 band of HOCO+ recorded with a 0.4 s time constant.

TABLE I. Molecular constants of HOCO$^+$ (in MHz).

	$v_1 = 1$ state	Ground state
A	754 611.2(86)[a]	788 794.2(65)
B	10 761.25(13)	10 773.66(11)
C	10 589.63(13)	10 609.38(11)
Δ_J	0.003 58(23)	0.003 41(17)
Δ_{JK}	0.080(44)	0.923(10)
Δ_K	359.1(25)	
Φ_{KJ}	− 0.105(11)	
v_0	101 191 174.7(76)	[3 375.374 26(25) cm^{-1}]

[a] One standard error to the last digits of the constants.

(10 773.66 ± 0.26 MHz) and C_0 (10 609.14 ± 0.22 MHz), obtained from the fit were in excellent agreement with those obtained by Bogey et al.[4] The molecular constants listed in Table I were obtained from a subsequent fit which included the microwave lines[1,4] in addition to the IR lines. The rotational constant A was determined precisely for the first time, and it is in good agreement with that calculated by DeFrees et al.[2] The band origin is found to be about 27 cm^{-1} higher than calculated by Frisch et al.[12] The δ_J and δ_K constants turned out to be insignificant, and were therefore neglected. We were forced to include Φ_{KJ} in the excited state to fit the $K = 0$, 1, and 2 lines at the same time. The rather large value of Φ_{KJ} and large differences of Δ_{JK} and Δ_K between the ground and the excited states may be indications of the quasi-linearity of this molecule, or of a Coriolis type interaction. A more complete analysis is in progress, and more extensive results will be published later.

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NO thermally desorbed from a saturation coverage on Pt(111): Internal state distributions

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Thermal desorption spectroscopy has become a major tool for determining activation energies and desorption mechanisms involved in adsorbate-surface-bond breaking processes.[1,2] Steady state thermodynamics are often applied to the interpretation of such experiments, ignoring dynamical aspects of the molecule–surface interaction. While a variety of more sophisticated theoretical approaches exist for dealing with the dynamics of desorption,[3,4] there has been only one experimental characterization of a desorption system at the quantum-state specific level.[5,6] That work studied the thermal desorption of NO from Ru(001) and found the rotational temperature of the desorbed NO to be only one half the temperature of the crystal. Although several statistical mechanical models have attempted to address this cooling factor,[7,8] it should be recognized that in the NO/Ru(001) system there is the potential for competition between molecular desorption and dissociation to form adsorbed N and O

atoms. The desorption of NO from Pt(111) is free of competitive processes such as dissociation or surface reconstruction and has been extensively studied by surface sensitive spectroscopies,[9] molecular beam scattering,[10] and conventional thermal desorption.[11] The desorption of NO from Pt(111) therefore represents a useful test case for probing the dynamics of an elementary thermal desorption process.

The experiments reported here used laser-excited fluorescence (LEF) to measure the density of desorbed NO species in a specific rotational (J), spin-orbit (Ω), and lambda doublet ($A^{\pm}$) level and to determine the alignment of these species.[12,13] The spin-orbit splitting in the NO ground $\tilde{X}^2\Pi_\Omega$ states is 124 cm^{-1} and results from an interaction between the unpaired electron spin and its orbital angular momentum. In the classical high J limit the lambda doublets are distinguished by the in-plane (A^+) or out-of-plane (A^-) spatial distribution of the partially filled π orbital with respect